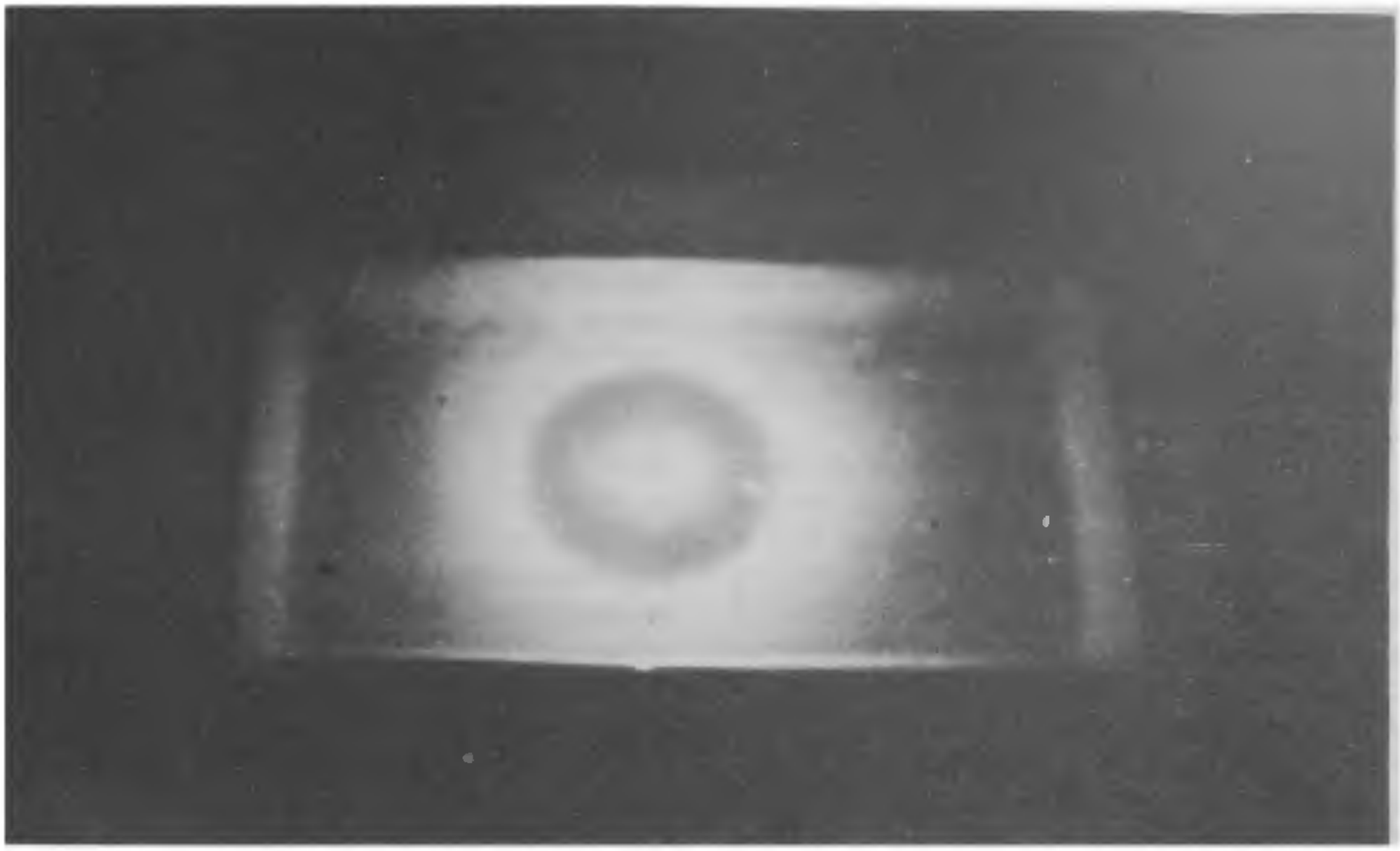

Figure 2. Photograph of circular ring pattern observed for water.

useful for volatile and acid media. The method is very practical for several quantitative studies such as variation of refractive index with temperature, refractive indices of liquid mixtures and solutions of different concentrations, opalescence properties, and so on.

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PMR SPECTRAL EVIDENCE FOR STERIC ENHANCEMENT OF RESONANCE

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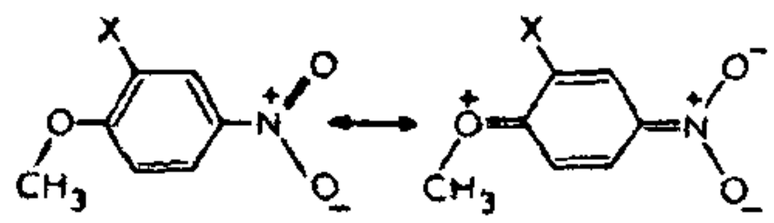
AFTER the discovery of steric enhancement of resonance[1], several studies[2–13] have afforded additional evidence for it. The present study, which deals with the PMR spectra of 2- and 2,6-disubstituted 4-nitroanisoles, and 2- and 2,6-disubstituted 4-carbomethoxyanisoles, provides further evidence for steric enhancement of resonance.

There is resonance interaction of the CH_3O- and $-NO_2$ groups in 4-nitroanisole. A substituent like a methyl group or a halogen atom in the 2-position (I) enhances the resonance by a steric effect.

The substituent X prevents the free rotation of the methoxy group and so the CH_3 of the methoxyl will be oriented away from X. Such a situation will increase the chances of the methoxyl attaining the plane of the benzene ring and consequently the resonance interaction of CH_3O- with $-NO_2$ also



I (X=CH_3, Cl, Br or I)

increases. It may be remembered in this context that the presence of substituents in the 2- and 6-positions causes the well-known steric inhibition of resonance because the methoxyl cannot then attain the plane of the benzene ring.

The methyl protons in 4-nitroanisole are more acidic than the methyl protons in anisole, because the nitro group is electron-withdrawing. This is reflected in the chemical shift of the OCH_3 protons in 4-nitroanisole. If there is steric enhancement of resonance in 2-substituted 4-nitroanisoles, the chemical shift of the OCH_3 protons in them should be still higher. This is indeed the case, as the values given in table 1 indicate. The chemical shift of 4.07 ppm of the methoxyl protons in 2-methyl-4-nitroanisole is higher than the chemical shift of 3.98 ppm of those in 4-nitroanisole, pointing to increased resonance in the former. The value of 3.92 ppm for 2,6-dimethyl-4-nitroanisole is lower than that (3.98 ppm) for 4-nitroanisole, showing the expected steric inhibition of resonance. The chemical shifts of 2-chloro-, 2-bromo- and 2-iodo-4-nitroanisoles also show steric enhancement of resonance of the CH_3O- group. It is, however, interesting to note that 2,6-dichloro, 2,6-dibromo and 2,6-diiodo compounds have values which are unexpectedly the same as or slightly higher than the value for 4-nitroanisole, while the 2,6-dimethyl compound, as expected, has a lower value than 4-nitroanisole. Understandably the methoxyl experiences non-bonded interaction with the halogen atoms in the 2,6-dihalogeno compounds and this results in the H atoms of the CH_3O- being attracted by the lone pair electrons of the halogen atoms. Consequently the distance between the bonding electrons and the H nuclei increases, some deshielding of H nuclei occurs, and the chemical shift of the methoxyl protons increases. But in the case of the 2,6-dimethyl compound there will be repulsion between the 2,6-dimethyls and the methoxyl methyl, and no attraction.

The behaviour of 4-carbomethoxyanisoles is akin to that of 4-nitroanisoles. What is said of nitroanisoles holds good for carbomethoxyanisoles.

Table 1 *PMR spectral data* of 4-nitroanisoles and 4-methoxycarbonylanisoles*

Anisole	Chemical shift of ^1H(ppm) in $-OCH_3$
Anisole	3.73
4-Nitro	3.98
2-Methyl-4-nitro	4.07
2,6-Dimethyl-4-nitro	3.92
2-Chloro-4-nitro	4.05
2,6-Dichloro-4-nitro	3.98
2-Bromo-4-nitro	4.08
2,6-Dibromo-4-nitro	4.00
2-Iodo-4-nitro	4.11
2,6-Diiodo-4-nitro	4.03
4-Carbomethoxy (4-COOMe)	3.91
2-Chloro-4-carbomethoxy	3.99
2,6-Dichloro-4-carbomethoxy	3.94
2-Bromo-4-carbomethoxy	4.02
2,6-Dibromo-4-carbomethoxy	–
2-Iodo-4-carbomethoxy	4.05
2,6-Diiodo-4-carbomethoxy	3.92

* All ^1H NMR spectra were recorded at room temperature in a Perkin Elmer R32 NMR spectrophotometer at 90 MHz frequency in $CDCl_3$ and are referenced to TMS.

8 February 1988

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SYNTHESIS OF SOME STYRYL DYES FROM 3-ETHYL-2-THIO-4-SELENAZOLIDONE

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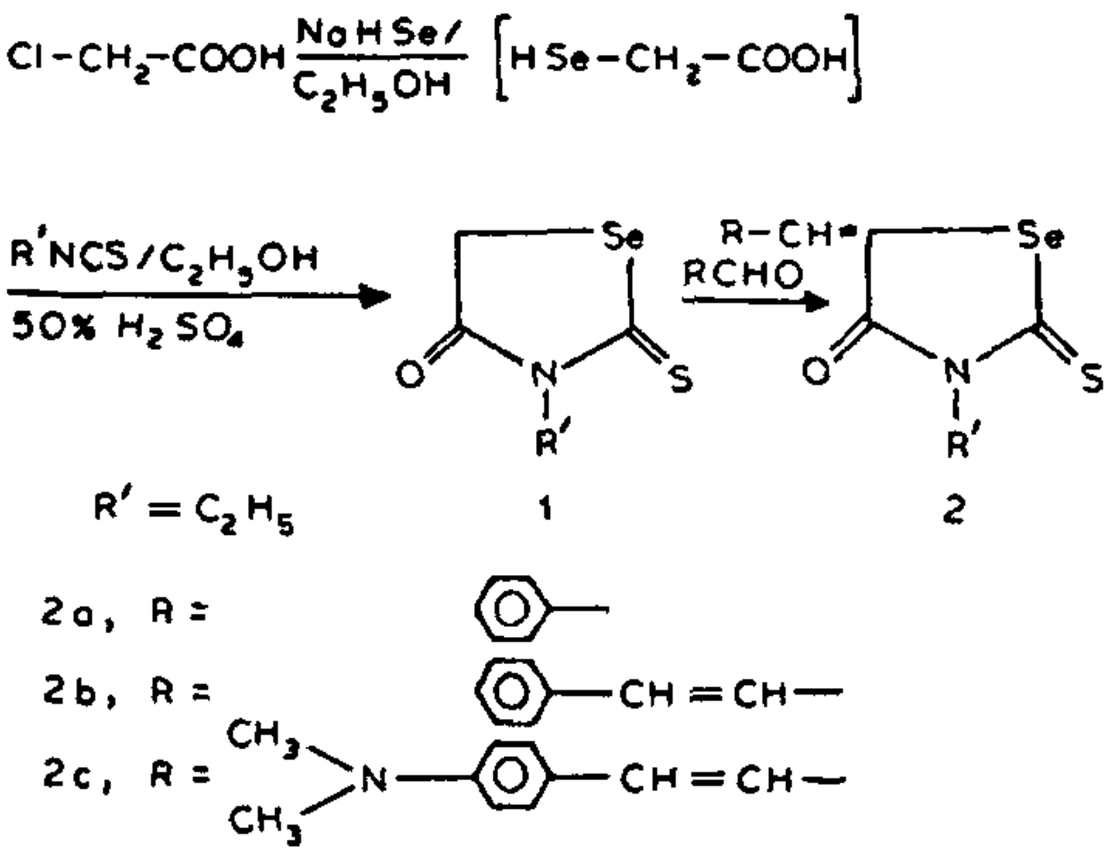
THE body of information found in chemical literature on the synthesis of 2-thio-4-selenazolidones[1,2] is meagre. A literature search was undertaken to synthesize some styryl dyes using thioselenazolidones. Surprisingly, no report has appeared hitherto on the syntheses of styryl dyes using the above mentioned selenium heterocycle. Incidentally the synthesis of thioselenazolidone itself appears to be accomplished by a circuitous method[1,2] which involves the reduction of diselenodiglycolic acid and a subsequent reaction of the resulting selenoglycolic acid with alkyl/aryl isothiocyanates. As the above method involves three steps viz. the preparation of diselenodiglycolic acid, its reduction to selenoglycolic acid and the final reaction of the same with appropriate isothiocyanates, we focussed our attention on the preparation of selenoglycolic acid through a simpler procedure. In this context, it is worth mentioning that the facile and easy preparation of sodium hydroselenide[3] *in situ* in ethanol solution and its reaction on organic compounds containing replaceable chlorine atoms have given impetus to numerous nucleophilic displacement reactions involving hydroselenide anion. Extending the above methodology to chloroacetic acid, selenoglycolic acid was prepared *in situ* which in turn was reacted with ethylisothiocyanate in the same pot to get 3-ethyl-2-thio-4-selenazolidone (1) in moderate yield.

Having achieved the one pot synthesis of the thioselenazolidone (1) our subsequent interest was to prepare some styryl dyes (2). They were synthesized by reacting thioselenazolidone with appropriate aldehydes in the presence of sodium hydroxide. The structures of the products were fully attested by elemental analysis and PMR spectral data.



Synthesis of 3-ethyl-2-thio-4-selenazolidone (1)

Chloroacetic acid (94.5 g, 1 mol) taken in ethanol (50 ml) was added dropwise to a freshly prepared sodium hydroselenide[3] solution, *in situ* in ethanol under nitrogen cover and was refluxed on a water bath for 2 h. After adjusting the pH of the solution to about 2 by adding 50% sulphuric acid, ethylisothiocyanate (85 g, 1 mol) was added in one lot and refluxed for 5 h. The reaction mixture was cooled, poured onto ice and extracted with chloroform. The chloroform layer was washed with water and dried (anhyd. Na_2SO_4). The solvent was removed under reduced pressure to get an oily liquid of thioselenazolidone which was further purified by vacuum distillation.

Yield: 83 g (40%); b.p. 120–125°C/12 mm;

PMR: (CCl_4) δ1.25(t, 3H, CH_2–CH_3, J = 6 Hz), 3.28(S, 2H, Ring CH_2) and 4.13(q, 2H, CH_2–CH_3, J = 6 Hz).

General procedure for the preparation of styryl dyes (2)

To a mixture containing equimolar quantities of 3-ethyl-2-thio-4-selenazolidone and appropriate aldehyde in ethanol (10 ml) was added 5 M aqueous sodium hydroxide (0.5 ml). The solution was left at room temperature for 2 h with occasional stirring. After the removal of ethanol the residue was extracted with ether. The ether layer was washed with saturated sodium bisulphite solution to remove the unreacted aldehyde and then with water and dried (anhyd. Na_2SO_4).. Removal of ether gave crude styryl dye which was further purified by passing through a silica gel column. The styryl dyes were recrystallized from appropriate solvents. The yield, m.p. and PMR data are given in table 1.