ing piperidine to compounds having two hetero-atoms. This can be attributed to the presence of the second heteroatom in the ring system and possibly through the inductive effect. The pK_a value of thiomorpholine further indicates that its basicity lies between those of piperazine and morpholine. In the case of thiomorpholine and morpholine, the decrease in the basicity is accounted for the existence of two n-electron pairs on the sulphur or oxygen atoms. Between thiomorpholine and morpholine, the former is slightly basic. This can be explained on the basis of: (i) Oxygen being more electronegative than sulphur, and (ii) Sulphur being of larger size than oxygen, as a result of which the lone pair repulsions become slightly less prominent as compared to the perturbation of the lone pair at the nitrogen atom of thiomorpholine.

The basicity of heteroalicyclic molecules in the excited singlet states cannot be predicted directly owing to the non-fluorescent nature of such molecules. However, in the present case, the Förster cycle method[10] is used to evaluate the pK_a value in the excited singlet state.

$$pK_a(S_1) = pK_a(S_0) - 2.1 \times 10^{-3}(\nu_A - \nu_B), \quad (2)$$

where ν_A and ν_B are the wavenumbers of the conjugate acid and base respectively. This value of 3.78 indicates that thiomorpholine cation becomes acidic upon excitation, corroborating earlier results in some imidazole derivatives[6].

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PHASE RULE STUDIES OF BINARY SYSTEMS INVOLVING SULPHOXIDES AND PHENOLS — AN INTERESTING CASE OF COMPOUND FORMATION

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WITH a view to studying the possible interaction between sulphoxides and phenols, the phase diagrams of eight binary systems, each consisting of a sulphoxide and a phenol, have been studied (table 1). The choice of the compounds was restricted as they have to be solids. All the systems except the one with methyl 4-nitrophenyl sulphoxide and p-nitrophenol form simple eutectics. Methyl 4-nitrophenyl sulphoxide and p-nitrophenol showed the formation of a compound with a congruent melting point at 104°C and an equimolar composition.

Having found from the phase diagram the formation of a compound between methyl 4-nitrophenyl sulphoxide and p-nitrophenol, the compound was prepared by mixing the components in 1:1 ratio (molar), melting, thoroughly mixing and solidifying the melt. It could be crystallized from benzene-petroleum ether (b.p. 70–80°C). Attempts to crystallize it from polar solvents like ethanol resulted in its dissociation into individual components. The compound melted at 104°C which is exactly the same as that shown by the phase diagram.

The IR spectrum of the compound and the spectra of the nitrophenol and sulphoxide, from which it is formed, were taken using methylene chloride as solvent. The characteristic bond frequencies are given in table 2. The data confirm the formation of the compound. The sulphoxide has a strong band due to S–O stretching at $1082\,cm^{-1}$ (Barnard *et al*[1] found a strong band near $1050\,cm^{-1}$ for sulphoxides). The $S \rightarrow O$ (or $S = O$) bond of the sulphoxide gives rise to two S–O bonds (S–OH and S–

Table 1 *Binary systems studied*

| Sulphoxide (m.p., °C) | Phenol (m.p. °C) | Eutectic point | |
		Temp. (°C)	Molar fraction of sulphoxide (%)
Di-*p*-chlorophenyl (143)	*p*-Nitro (114)	51	59
Di-*p*-chlorophenyl (143)	2,4,6,-Trinitro (122)	92	63
Methyl *p*-nitrophenyl (147)	2,4-Dinitro (113)	81	61
Methyl *p*-nitrophenyl (147)	2,4,6-Trinitro (122)	79	40
Methyl *p*-nitrophenyl (147)	*m*-Nitro (96)	26	60
Methyl *p*-nitrophenyl (147)	3,4-Dimethyl (64)	20	70
Methyl *p*-nitrophenyl (147)	*p*-Nitro (114)	98	42
		76	77
Methyl *p*-nitrophenyl (147)	*β*-Naphthol (122)	56	51

$O.C_6H_4-p$) in the compound (I) formed and absorption was found in the region 1080–1035 with a maximum at $1042 \, cm^{-1}$. This shows that the sulphoxide group has undergone a change. Significant differences were also found in the OH stretch-

Table 2 *Characteristic IR bands of the groups*

Group	Mode of vibration	Frequency (cm^{-1})
p-Nitrophenol		
OH	Stretching	Broad band, 3620–3515 max. at 3525
OH	Deformation	878
NO₂	Asymmetric	1515
NO₂	Symmetric	1335
NO₂	Deformation	864
Methyl *p*-nitrophenyl sulphoxide		
NO₂	Asymmetric	1525
NO₂	Symmetric	1345
NO₂	Deformation	866
SO	Stretching (–SO–)	1082
Compound of 1 & 2 (I)		
OH	Stretching	Broad band, 3580–3320 no sharp max.
OH	Deformation	875
NO₂	Asymmetric	1524
NO₂	Symmetric	1343
NO₂	Deformation	866
SO	Stretching, Two S–O bonds exist $\equiv$S–OH | OAr	Broad band, 1080–1035 due to overlapping max. at 1042

ing and deformation frequencies of nitrophenol and those of the compound. In the former the OH is attached to the benzene ring and in the latter it is attached to the S atom.

It is significant that 2,4-dinitrophenol or 2,4,6-trinitrophenol, which are more acidic than *p*-nitrophenol, did not form a compound with methyl *p*-nitrophenyl sulphoxide. It may also be noted that a nitro group, para to the sulphoxide group is necessary for compound formation. The nitro group, being electron-withdrawing, increases the positive charge on the sulphur atom. Considering the above facts the possible structure for the
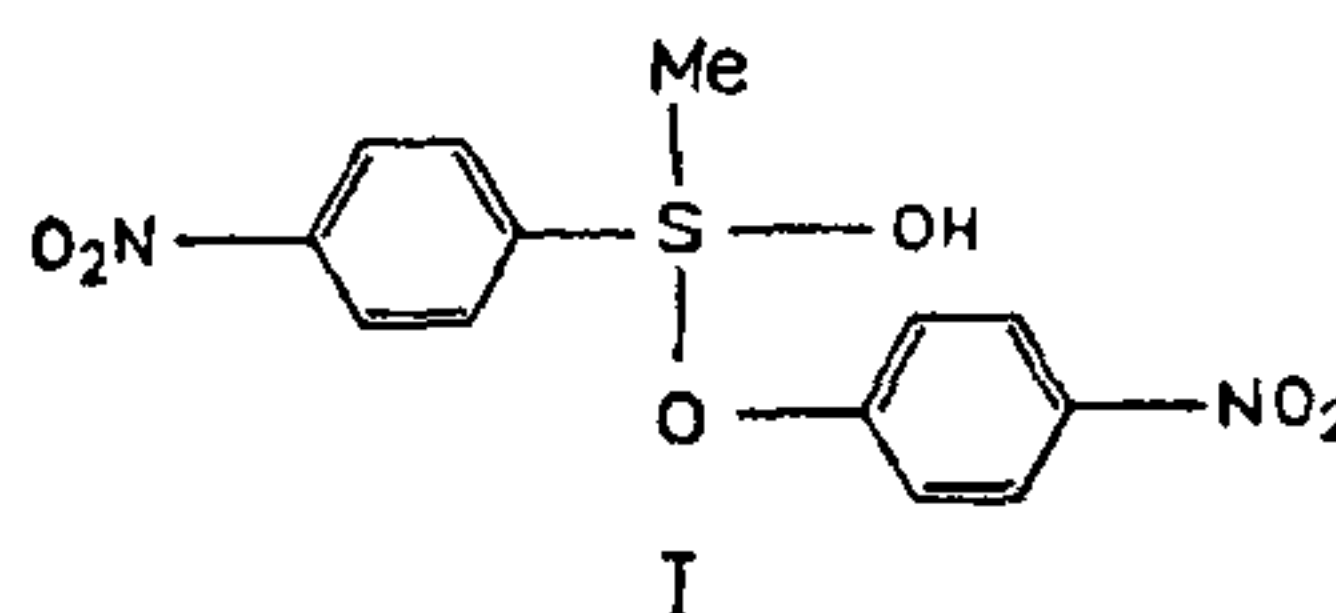
compound is I. Such a compound-formation is made possible by the ability of sulphur to expand its valency shell by the utilization of its vacant *d*-orbitals. The enhanced positive charge facilitates the formation of a new S–O bond between sulphur and the negatively-charged oxygen of the phenoxide ion which results by the bonding of the easily liberated proton from the phenol with the oxygen of the sulphoxide. 2,4-Dinitrophenol and 2,4,6-trinitrophenol, though more acidic than *p*-nitrophenol and can give anions more easily, failed to form a compound because the linking of sulphur with the negatively charged phenolic oxygen is presumably hindered sterically by the ortho nitro group or groups of the phenol.

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RELATIVE SENSITIVITY OF ANGIOSPERMIC POLLEN TO ENDOSULPHAN

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PESTICIDES play a vital role in crop protection, but at times they cause phytotoxic effects such as stunting of growth, scorching of foliage, abnormal development of flower, inhibition of pollen germination/tube growth and reduced seed setting[1,2]. To ensure safe use of pesticides during flowering and seed formation, a simple system is required to evaluate toxicity and predict impairment in the reproductive process which seriously affect the ultimate productivity.

The use of pollen grains provides a convenient system for monitoring atmospheric pollutants[3], bioassay for toxic substances[4] and studies on mutation[5]. Some studies are available on the effect of pesticides applied as vapour or liquid spray during flower development yielding less viable and damaged pollen grains[6-9]. The effect of endosulphan on the pollen germination of *Catharanthus roseus* (Linn.) G. Don. was reported earlier[10] and this communication deals with the response of another three angiospermic plants viz. *Vigna radiata* (Linn.) Wilczek; *Trigonella foenum-graecum* Linn. and *Brassica campestris* Linn.

The pollen grains were collected from mature anthers early morning just before dehiscence. The effects of endosulphan were studied by sowing the pollen grains on sterilized cavity slide in drops (≈ 50 μl) of 10% sucrose culture media containing endosulphan in concentrations ranging from 10 to 1000 ppm. The slides so prepared were incubated for 4 h in a petri plate lined with moist filter papers at room temperature of 22–30°C and relative humidity of 49–70% under diffuse light. Parallel control experiments were conducted without endosulphan. After incubation, the pollen cultures were scanned under light microscope in ten fields (15 × 10 magnification) to determine germination and measure the pollen tube length by calibrated ocular micrometer.

Table 1 gives comparative data of percentage pollen germination in *C. roseus*, *V. radiata*, *T.*

Table 1 *Behaviour of pollen germination after premixing endosulphan in 10% sucrose culture media*

Endo-sulphan concen-tration (ppm)	Pollen germination (%)			
	C. roseus	*V. radiata*	*T. foenum-graecum*	*B. campestris*
0	85	88	95	85
10	65 (24)	75 (12)	70 (33)	55 (35)
100	45 (47)	50 (41)	25 (76)	20 (76)
500	10 (88)	20 (67)	5 (95)	NG (100)
1000	NG (100)	5 (94)	NG (100)	NG (100)

The values are mean of 10 replicates; Figures in parentheses indicate percentage of inhibition; NG, No germination.

foenum-graecum and *B. campestris* on treatment to varying endosulphan concentrations. There was a drop in germination with increase in concentration of the insecticide. At 500 ppm the pollen of *B. campestris* failed to germinate while in the other three species germination was uniformly low. *Catharanthus* and *Vigna* pollen were more resistant than *Trigonella* and *Brassica* as the percentage inhibition in germination was more severe in the latter group.

Table 2 shows pollen tube growth in different species after endosulphan treatment. The pattern of inhibition in tube growth was similar to that found in germination in response to different concentrations of endosulphan. However, the degree of inhibition was more severe in tube growth than in germination. The present observations support the view that pollen germination and tube growth are independent processes governed by separate conditions[11]. Of the two processes the activation phase of pollen germination was less sensitive to endosulphan. Some effects were also observed on the initiation phase as the time for sprouting was delayed (data not presented in tables) with increasing endosulphan concentration in the treatment medium. However, severe effects were observed on the exponential phase.

The mechanism of inhibition of pollen germination and tube elongation is not clear but by equating with some of the known phytotoxic effects of endosulphan on seed germination and seedling growth[12-14] a plausible explanation may be offered.