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ROTATIONAL ISOMERISM IN BENZIL

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THE molecular configuration of benzil has been a subject of considerable interest and was investigated by several workers, by different methods, *viz* dipole-moment¹, x-ray diffraction², IR³⁻⁵, UV⁶, NMR⁷, molar refractivities and Kerr constants⁸. It was established that the molecule is not planar and has a skew configuration with the two carbonyl groups making an angle of 90°–100° and that the two benzene rings are twisted by 5.1° from the carbonyl planes. But from the study of IR spectra in nujol and decalin, Sterk⁴ had shown that at higher temperatures two different conformations exist with quasi-cis-trans character. As nothing has been reported about the existence of more than one conformer in solution at room temperature and the influence of solvents on the relative stabilities of the conformations, it was considered useful to carry out the work on these aspects and the results of the investigations are reported in this communication.

IR spectra of equimolar solutions of different protic

and non-protic solvents of different dielectric constants were recorded at slow speed on Perkin Elmer 337 grating spectrophotometer at 28°C using NaCl matched cells of 0.5 mm path length. The spectra g & h (figure 1) were recorded as binary solvent mixtures (Phenol/Pyrrole + CCl₄) on Perkin Elmer 283 grating spectrophotometer. In carbontetrachloride benzil exhibited two carbonyl bands at 1672, 1682 cm⁻¹. Similar observation was also made by Bernal⁵ who attributed the splitting of the band to C₂ symmetry of the molecule. If this is true, similar splittings are expected in anisil and furil which also have the same symmetry. They however exhibit sharp singlets⁹.

In carbontetrachloride the intensity of the lower frequency band is greater than that of the higher frequency band. The relative intensities did not suffer any change with change in concentration of benzil. The splitting of the carbonyl band, therefore, is not due to the intermolecular interactions. However, the relative intensities of the bands changed with change in polarities of the solvents (figure 1). This pattern of intensity variation of the doublet is quite analogous to that observed in the case of chloroacetone¹⁰ and *o*-bromo acetophenone¹¹ which are known to exhibit rotational isomerism. The two carbonyl bands of benzil are therefore due to two rotational isomers of the molecule. The rotamer stabilized in more polar solvent (acetonitrile) should have a large dipole-moment. This may be the cis form in which the two carbonyl groups of benzil are in eclipsed position. The carbonyl frequency of such a rotamer is expected to be higher due to field inductive effect. The rotamer with preferential stability in carbontetrachloride should obviously have smaller dipolemoment. This could be the skew form which has lower carbonyl frequency. The higher frequency band is therefore assigned to the cis form and the lower frequency to the skew form. Thus, in all the solvents used, benzil at room temperature exists as an equilibrium mixture of two rotamers, *viz* the skew and the cis, with the cis form predominating in solvents of larger polarities as is evident from the cis/skew ratio (table 1).

The influence of protic solvents like phenol and pyrrole on the relative stabilities of the two rotamers is examined as binary solvent mixtures. In the presence of a small quantity of phenol (or pyrrole) in carbontetrachloride the intensity ratio of cis/skew increased showing the relative stabilization of the cis rotamer. The stabilization of the cis form in phenol/pyrrole is attributed, besides dielectric effect, to the formation of bifurcated H-bonds between phenolic OH (or NH of pyrrole) and the two carbonyl groups (figure 2).

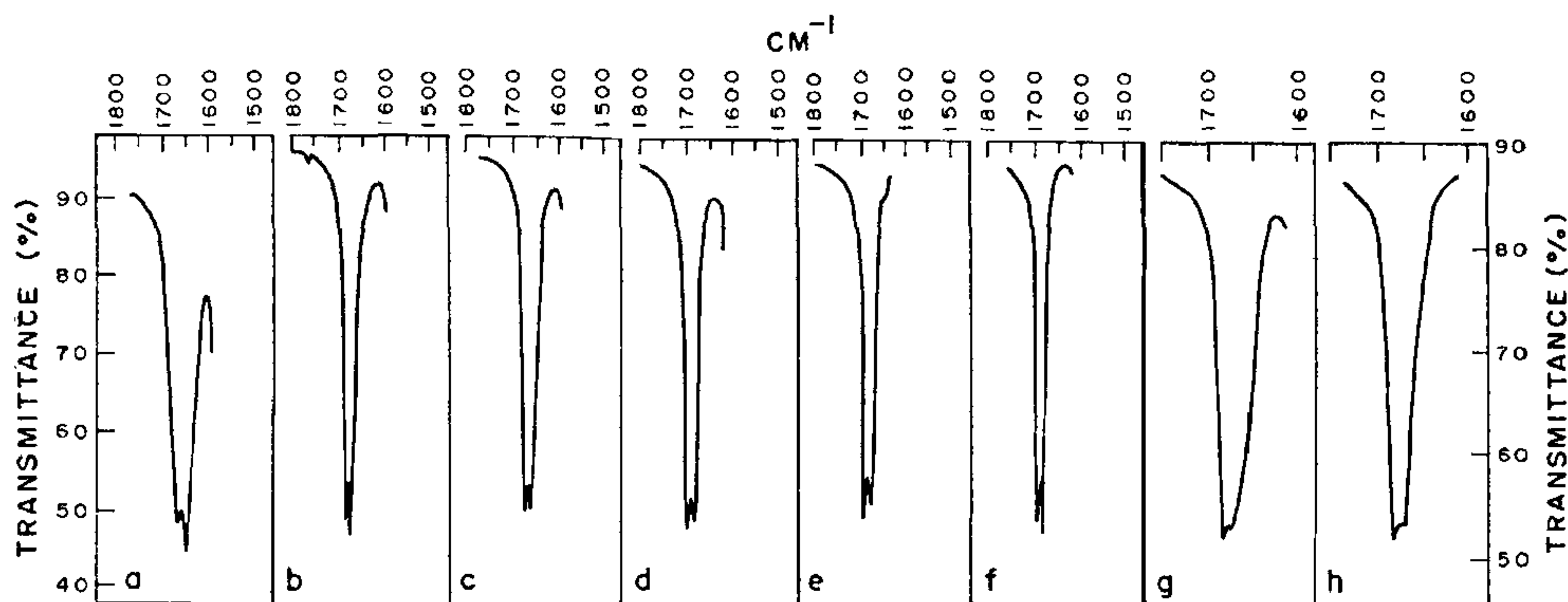


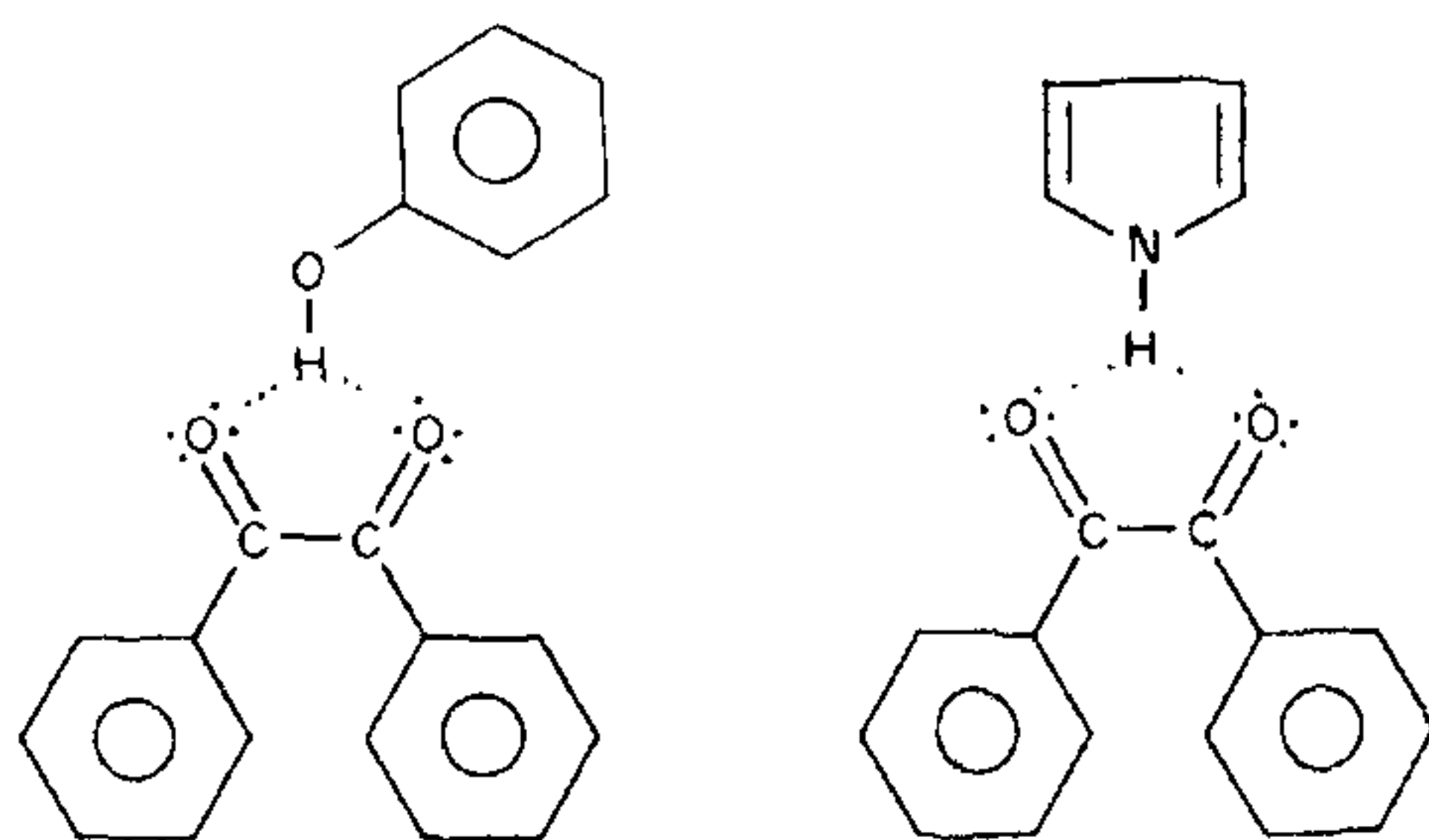
Figure 1. C = O bands of benzil in different solvents (a) KBr (b) CCl₄ (c) CHCl₃ (d) CH₂Cl₂ (e) CH₃CN (f) CCl₄ + Anisole (g) CCl₄ + Phenol (h) CCl₄ + Pyrrole.

Table 1 Frequencies (cm⁻¹) and Relative intensities of the C=O Bands of Benzil

	KBr	CCl ₄	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN	Pyrrole*	Phenol*
	1675	1682	1681	1680	1680	1679	1677
	1656	1672	1671	1670	1670	1670	1670
Cis/Skew† ratio	0.910	0.971	1.007	1.018	1.053		

* Binary solvent mixtures.

† The ratios were obtained from the relative optical densities of the high and low frequency bands as the measurements of integrated intensities of the bands is prevented by extensive overlap of the bands.



This is also evident from the spectra of dilute solutions of mixtures of benzil and phenol (or pyrrole) in the 3 μ region (figure 3) which exhibit bonded OH or NH bands, besides the respective free (unassociated) bands. It may appear that the stabilization of cis form by pyrrole is due to the dielectric effect as its dielectric constant (7.47) is nearly the same as that of methylene chloride (9.1). In such a case the cis/skew ratios in these two solvents should be nearly the same with the

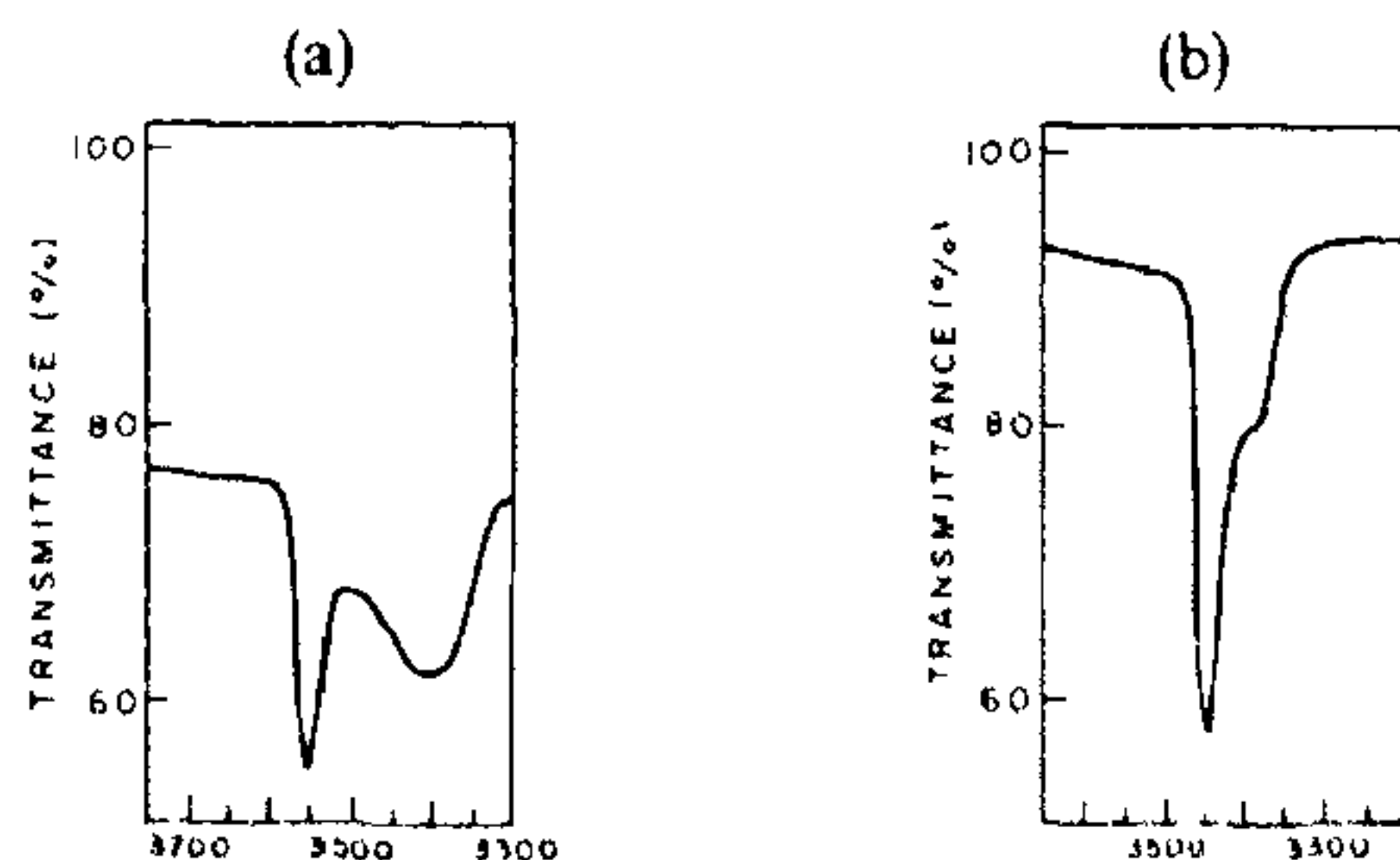


Figure 3. (a) Phenol and Benzil mixture in CCl₄. (b) Pyrrole and Benzil mixture in CCl₄.

value in pyrrole slightly less than that in methylene chloride. But the ratio in pure pyrrole (1.51) is far higher than that in methylene chloride (1.018) showing that H-bonding effect also plays quite a significant part in stabilising the cis form.

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OCCURRENCE OF HIGHLY ACIDIC GROUNDWATER IN MULUG TALUK, WARANGAL DISTRICT, ANDHRA PRADESH, INDIA

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DURING the hydrogeological inventory in the Lower Maner Basin in Warangal district, Andhra Pradesh, an interesting occurrence of highly acidic groundwater was encountered.

The source of the groundwater sample was an open well belonging to Shri D. Chinna Mallaiah in the village Tachindlapet (18° 09' 49" N: 80° 00' 46" E) locally known as Kasimdevpet in Mulug Taluk, Warangal district, Andhra Pradesh. The well is located in a topographic low in shale formations and is circular in shape with a diameter of 8.4 m. It is lined with stone work down to 8.5 m below ground level

(BGL) The total depth of the well was 8.5 m BGL. The water table was around 5 m BGL. The water had a greenish yellow colour and sulphur smell. Sulphur encrustation was seen around the well. Other available wells examined in the area showed a pH of 7.5 to 7.8, whereas the well waters under question are highly acidic.

The formations encountered in the well as well as in the environs are Mulug shales within the Mulug Group of Pakhal Super Group (Upper Pre-Cambrian). The shales are dark grey, laminated and micaceous. Occasional graphitic material was also seen. The shales exhibit weathering along bedding and joint planes.

The well was excavated for irrigation purpose. However, the plants could not be grown and frogs were also seen to die in this water.

A water sample was collected on 1.2.1975 and analysed at the site for pH and other perishable ions. Stable ions were later determined in the laboratory. The analytical results are given in table 1. Repeat analysis of a water sample collected on 10.5.1984 from this well gave a pH of 3.1 and EC of 4840 micromhos at 25°C.

Table 1 Chemical character of the acid water from a dug well in Tachindlapet

pH	: 3.2	Chloride	: 113 mg/l
Temperature	: 26 C	Sulphate	: 3122 mg/l
E.C. in micromhos, cm at 25°C	: 4177	Fluoride	: 31 mg/l
Total hardness as CaCO ₃	: 955 mg/l (mg litre)	Calcium	: 201 mg/l
		Magnesium	: 110 Mg/l
Total acidity as CaCO ₃	: 1013 mg/l	Sodium	: 540 mg/l
Carbonate	: Nil	Potassium	: 45 mg/l
Bicarbonate	: Nil	Iron	: 0.42 mg/l
		Silica	: 116 mg/l

From the analysis, it is inferred that pyrite which was available in the shales was getting oxidised and in the process releasing sulphurous acid. The sulphurous acid is further oxidised to sulphuric acid. Other wells in the area (nearest one was 800 m away towards NW), however, showed a pH of 7.5 to 7.8. Because this was an isolated case of such highly acidic waters, it is surmised that a local enrichment of sulphide minerals may have contributed to this acidity.

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