

STEREOSPECIFIC SYNTHESIS OF
(Z)-M-1-BROMO 1-PHENYL-2-*p*-TOLYL-
SULPHONYLETHYLENE

FOR our current investigation on the synthesis and structural studies of some E-*a*M, E-M and Z-M unsaturated sulphide-sulphones and disulphones, we were interested in preparing a *cis* (with respect to *p*-CH₃C₆H₄SO₂ and Br) (Z)-M-1-bromo-1-phenyl-2-*p*-tolylsulphonylethylene as a starting material. Amiel¹ reported the synthesis of a compound with a similar configuration with very poor yields, the *trans* isomer forming the major product. According to our procedure the *cis* (Z) isomer in a very high yield is formed.

Recent studies^{2,3} have confirmed that the nucleophilic addition of sodium thiolates to acetylenic hydrocarbons proceed in the *trans* fashion to yield *cis* compounds. Thus *cis*- ω -styryl *p*-tolyl sulphide (I) was prepared by the reaction of an alcoholic solution of phenylacetylene with sodium *p*-toluene thiolate.

It is well known that the addition of halogens to olefins is stereospecific, *trans*-olefin leading to the formation of a non-resolvable *meso* form (*erythro*) and *cis* isomer leading to the formation of a resolvable racemic (*d, l*) form (*threo*)⁴. The *cis* isomer (I), on bromination in carbon tetrachloride produced a *threo d, l*-dibromide (II) which on dehydrobromination with diethylaniline in carbon tetrachloride yielded a *cis* (with respect to *p*-tolyl-S and Br) olefine (III). This is in analogy with the compound obtained by dehydrobromination of *threo*-benzalacetophenone dibromide reported by Lutz and his co-workers⁵. The compound III, on oxidation, gave *cis* (with respect to *p*-CH₃C₆H₄SO₂ and Br) (Z)-M-1-bromo-1-phenyl-2-*p*-tolylsulphonylethylene (IV).

Experimental

The elemental analyses were performed by Dr. R. D. MacDonald, CSIRO, Australia, The UV, IR and NMR spectra were determined with a ECIL UV-spectrophotometer, a Carl-Zeiss UR-10 Jena 242506 IR spectrophotometer and a varian A-60 NMR spectrometer respectively. The purity of the compounds was ascertained by TLC using silica gel G as the stationary phase and CHCl₃ : EtOAc (95 : 5 solvent layer) as mobile phase.

Phenylacetylene was prepared according to the procedure of Wittig and Witt⁶, b.p. 142-144° (lit⁶, b.p. 142-144°) and *cis*- ω -styryl *p*-tolyl sulphide was prepared as reported⁷, m.p. 63-64° (lit⁷, m.p. 64-65.5°).

(Z)-M-1-Bromo-1-phenyl-2-*p*-tolylsulphonylethylene (IV)

To a solution of 22.6 g (0.10 mole) of *cis*- ω -styryl *p*-tolyl sulphide in 100 ml of CCl₄, 16 g (0.1 mole) of bromine in CCl₄ was added dropwise at 15-20°. To the resulting brown solution, 20 g (0.1 mole) of diethylaniline was added and refluxed for 3h. The reaction

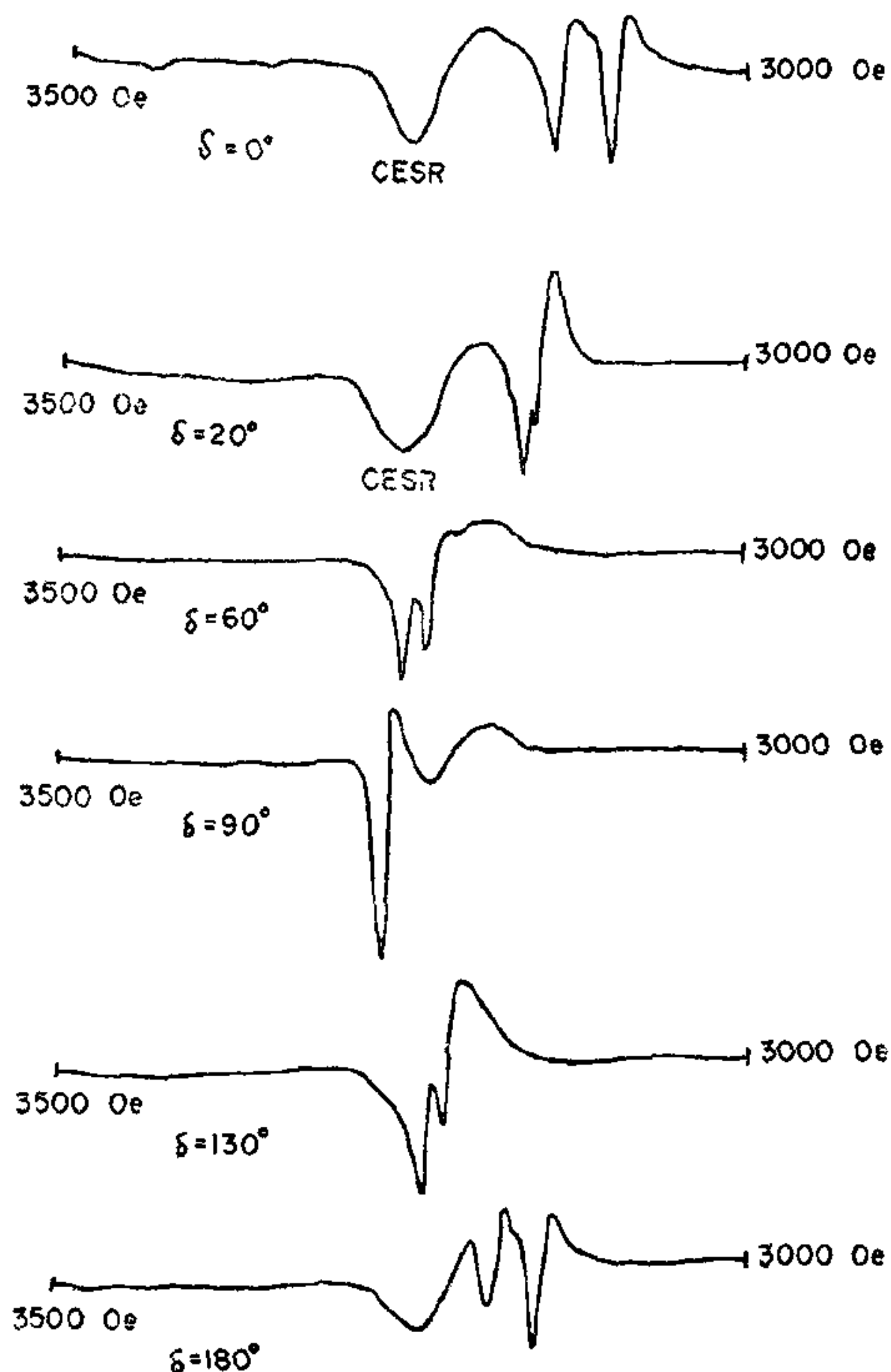


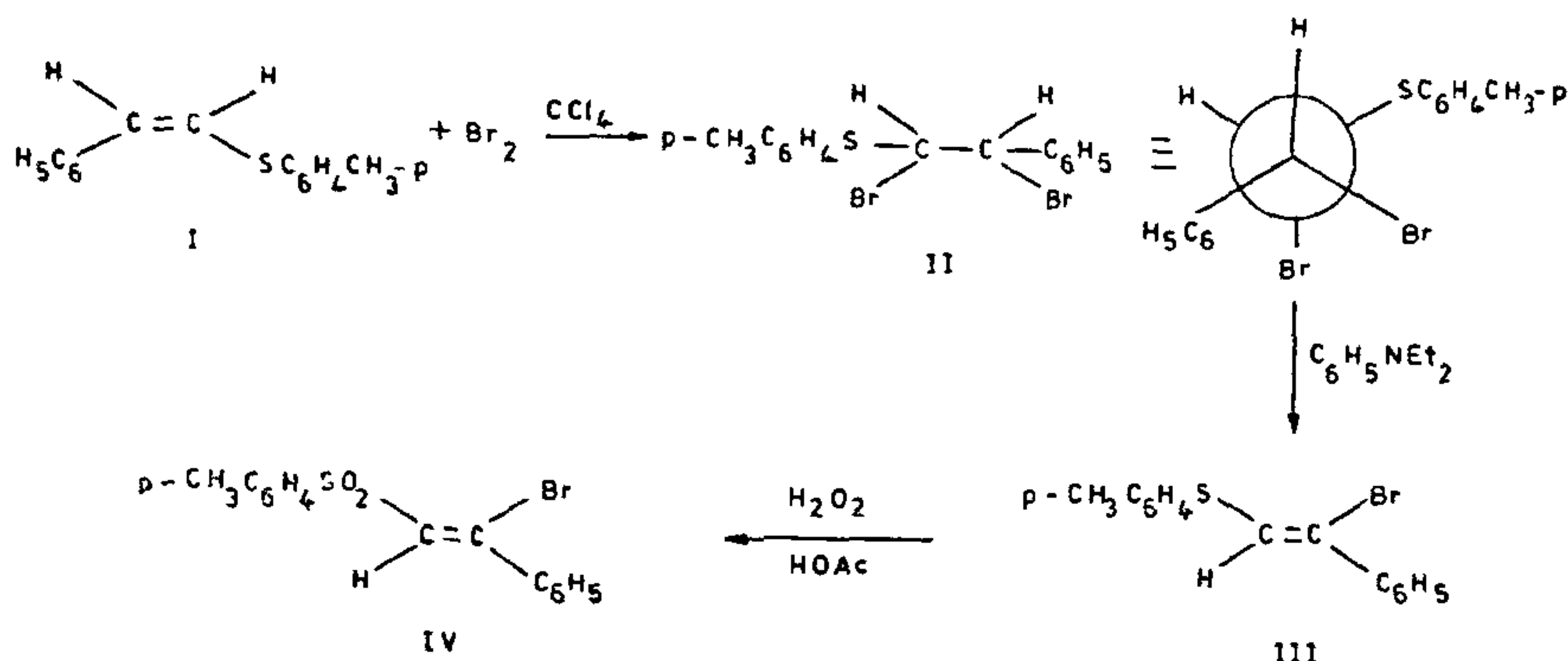
FIG. 2. CESTR and spin wave resonance as a function of the orientation of the applied field (δ).

Our observations, establish for the first time, the presence of antiferromagnetic interactions in conduction band as responsible for electron pairing.

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mixture was washed with dilute HCl followed by water. The solvent was removed under vacuum to yield (Z)-M-1-bromo-1-phenyl-2-p-tolylthioethene (III) (25 g, 80%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{SBr}$: C, 59.00; H, 4.29. Found: C, 59.20; H, 4.20.

To a refluxing solution of 3 g of crude III in 20 ml of glacial AcOH, 16 ml of 30% H_2O_2 was added. The reaction mixture was refluxed for one hour and poured into crushed ice. The separated product was filtered (yield 2.5 g, 75%) and recrystallized from 2-propanol. Two more recrystallizations of the compound from 2-propanol gave an analytical sample of (Z)-M-1-bromo-1-phenyl-2-p-tolylsulfonylethylene (IV) m.p. 110-111.5°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{SO}_2\text{Br}$: C, 53.40; H, 3.89. Found: C, 53.42; H, 3.91. UV $^{\text{ethanol}}_{\text{max}}$

204 nm (60, 770), 274 (48, 620); IR $^{\text{Nujol}}_{\text{max}}$ 3220, 3160, 2150, 1955, 1745, 1715, 1640 (C=C), 1615, 1535, 1550, 1530, 1470, 1450, 1445, 1385, 1365, 1335 (s) (SO_2 assym.), 1290, 1270, 1255, 1235, 1165, 1155 (s) (SO_2 sym.), 1120, 1080 (s) (S-aryl), 1055, 990, 968, 955, 945, 935, 900, 855, 840, 808 (s) (δ C-H out-of-plane) and 770 cm^{-1} ; NMR δ (CDCl_3) 2.45 (s, 3H, Ar-H), 7.30 (s, H, Vinyl-H), 7.65 (m, 9H, Ar-H).

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AVAILABILITY OF NITROGEN FIXING BLUE-GREEN ALGAE IN THE RICE FIELDS OF SOME DISTRICTS OF BANGLADESH IN DIFFERENT SEASONS

Introduction

CONVERSION of molecular nitrogen into organic form by photosynthetic plants is a significant and direct method of utilizing solar energy to convert atmospheric nitrogen into available form as food and feed. All heterocystous members, and some non-heterocystous members, of blue-green algae possess the ability to fix atmospheric nitrogen. Considerable work has been done on the utilization of this group of algae¹⁻⁶. Information on the availability of blue-green algae in different seasons, in Dacca District, has been reported earlier⁷. Reports on the occurrence of this group of algae in different seasons, in other districts of Bangladesh are not available. The present study was therefore undertaken to provide information on this aspect.