luminated with near UV light (peak output at 365 nm) for 20 min. The dose of near UV light used for photoprotection was 8×10^4 ergs/mm^2. Since there was no detectable growth at 5°C, experiments were conducted in which all holdings and illumination procedures were done at this temperature. Induction was started immediately after UV irradiation and the level of induced enzyme was determined at different time intervals. The results are presented in figure 1. Unilluminated cells held at 5°C for 20 min synthesized L-arabinose isomerase upon induction at the same rate as the cells which were not held. Near UV light exposure at 5°C (without UV irradiation) inhibited L-arabinose isomerase synthesis by nearly 50%. Cells irradiated with UV light at room temperature without prior cooling and holding synthesized the enzyme at a reduced rate up to 90 min after which it increased strikingly as the recovery phase began. When cells were held at 5°C for 20 min and then irradiated with UV light, L-arabinose isomerase induction occurred at a rapid rate up to 60 min, the rate dropped off after that and became almost similar to that in UV irradiated cells without any prior treatment. The cells which were given near UV light treatment for 20 min at 5°C and then irradiated showed an increase in the rate of L-arabinose isomerase synthesis up to 70 min and then the enzyme synthesis ceased for a shorter period, only to begin again after 90 min.

Thus it is clear that exposure of cells to near UV light by holding them at 5°C or only holding them at 5°C prior to UV irradiation protected them from the inhibitory effect of UV light on the L-arabinose isomerase synthesizing system (figure 1). These results are similar to those observed in the case of β-galactosidase synthesis[4]. The pattern of L-arabinose isomerase synthesis in cells photoprotected at 5°C (figure 1) is similar to that obtained from cyclic AMP treatment after UV irradiation[1]. It appears that irradiated cells were able to maintain cyclic AMP levels when given these treatments.

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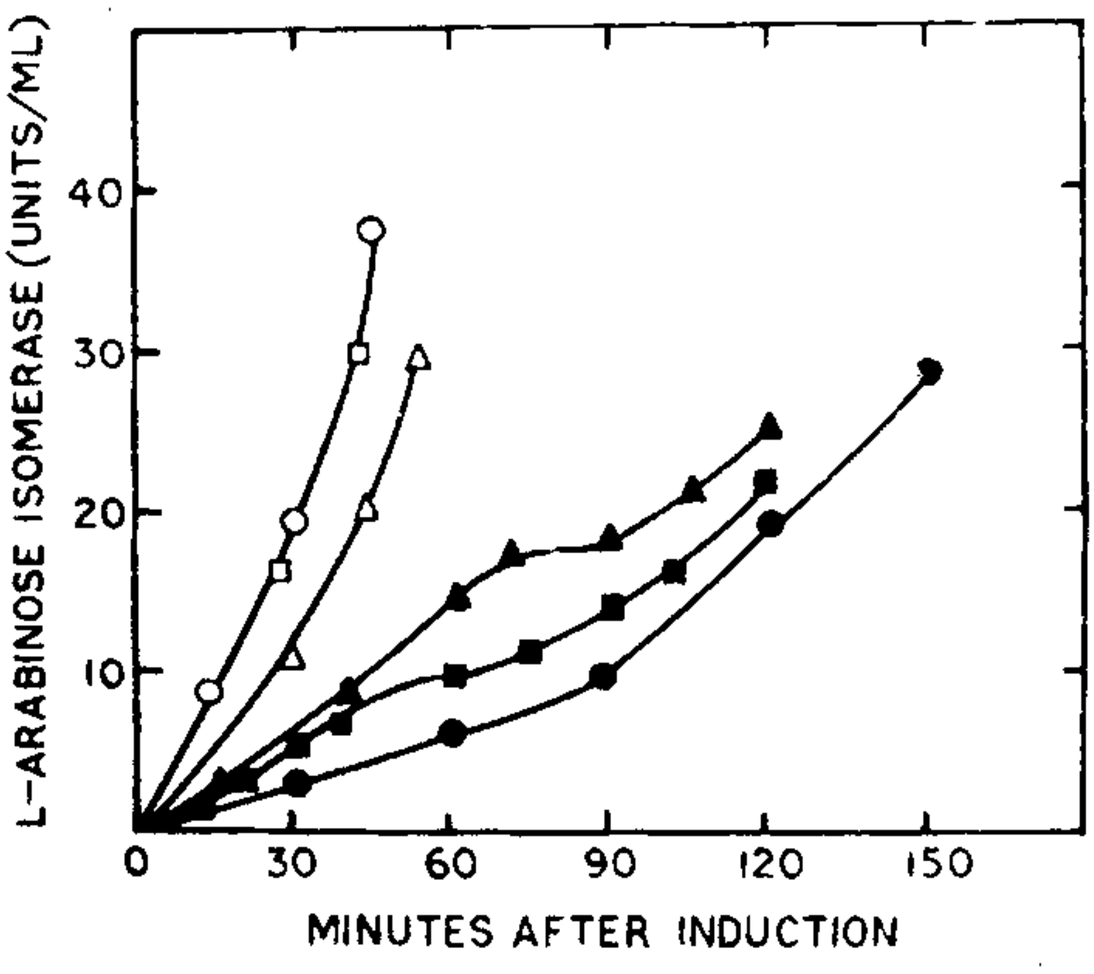

Figure 1. Effect of near UV light exposure to cells prior to far UV irradiation on the induction of L-arabinose isomerase. The level of the enzyme was determined at different time intervals after the addition of L-arabinose (1.33×10^{-2} M) in tris-EDTA treated *E. coli* B/r cells which had been unirradiated (○), unirradiated and held at 5°C(□), illuminated by near UV light (365 nm) at 5°C (△), irradiated with far UV light (254 nm) (●), and irradiated with far UV light after holding them at 5°C with (▲) and without (■) illumination by near UV light.

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SYNTHESIS AND INVESTIGATIONS OF THE NEW ADDUCT OF S_4N_4

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THE halogen derivatives of S_4N_4 and their complexes with metal compounds have been reported[1-9]. But an adduct of S_4N_4 with H_2F_2 is neither prepared and studied nor has it been used as a ligand to prepare its complexes. The new adduct of S_4N_4, nominated as tetrathiazyl dihydrofluoride is synthesized and is reported here.

Tetrathiazyl dihydrofluoride (TTADHF) was prepared by passing dry hydrogen fluoride gas into benzene solution of S_4N_4, which was prepared by Goehring's method[8], at 290 K with constant stirring for 4 to 5 hr till it was red. The reddish yellow mass was separated and washed with benzene to free it from S_4N_4 and dried in a vacuo.

TTADHF was analyzed qualitatively and quantitatively with the help of atomic absorption spectrum and gravimetric methods[9]. Its molecular weight was determined by Rast's method. IR (KBr pallet) and UV (reflectance) spectra were carried out on Perkin Elmer-257 and VSU-22 spectrometers respectively. Electron paramagnetic resonance spectrum of the tetrathiazyl hydrofluoride (TTADHF) was recorded on X–E–4 band EPR spectrometer at 300 K using DPPH as the internal standard. TTADHF was also tested against gram-negative and gram-positive bacteria using *in vitro* method.

The analytical data are: found S, 56.90%, N, 25.10%, F, 17.10%, H, 0.90%; while those calculated for the proposed molecular formula, $S_4N_4H_2F_2$ are; S, 57.0%, N, 25.13%, F, 16.95%, H, 0.90%. The molecular weight is found to be 224.5 which is in close agreement with the theoretical value of 224 for the aforesaid formula. Its melting point is 105°C.

The IR spectrum of TTADHF is compared with the spectra of S_4N_4 and $S_4N_4H_4$ and it is observed that the IR spectrum of TTADHF shows band at 540, 600, 719, 798, 920, 940, 1105, 1220, 1392, 1655 and 3180–3500 (b) cm^{-1}. Out of this 540 and 600 cm^{-1} assignments correspond to S–S bands while 719 and 920 cm^{-1} are for free S–N vibrations. 1105 and 1220 cm^{-1} show the presence of N–S–F bands and the frequencies 1392, 1655 and 3180 cm^{-1} are due to to S–N–H bands. The broadness of the last band (3180–3500 cm^{-1}) suggests the presence of hydrogen bonding in it. The bands 798 and 940 cm^{-1} have been deformed indicating that two S–N bands have symmetrically linked to other groups.

From the electronic spectrum of TTADHF, oscilator strength (f), bandgap energy (ΔE) and conductivity (λ_a) were determined. The two peaks at 24390 (v_1) and 33898 (v_2) cm^{-1} are found in its spectrum. The former vibration is due to σ bond while the latter is according to charge transfer environment which may be on account of the hydrogen bonding in it. Although the value of f 8.29×10^{-4} infers about the spin-allowed Laporate forbidden transition in it, the values of ΔE 1.17 and 3.39×10^{-20} suggest that TTADHF is a semiconductor.

EPR spectrum of TTADHF possesses a single peak

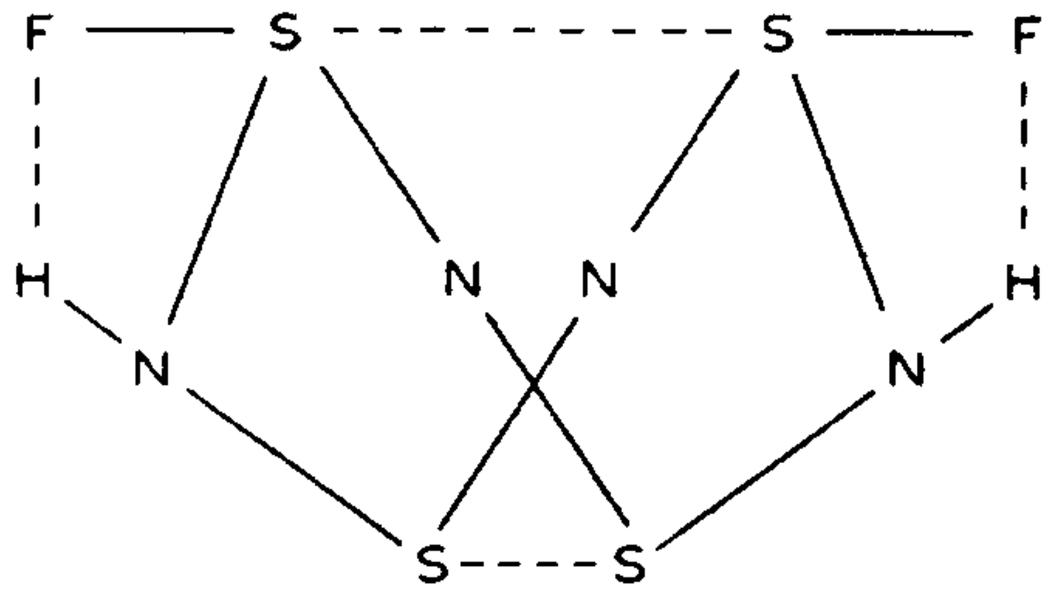

Figure 1. Proposed structure of $S_4N_4H_2F_2$.

of high intensity indicating the presence of unpaired electron in it. Other tensors such as μ_{eff}, g, A_H and λ_s are calculated and the values of $g = 1.994$, $\mu_{eff} = 1.73$, $A_H = 40$ and $\lambda_s = 19.79$ (cm^{-1}) are according to empty shells, single electron, electron interaction and slight spin orbital coupling in the compound respectively. The compound shows paramagnetism which is supported by its value for magnetic susceptibility ($\chi_A = 1.23 \times 10^{-3}$). The presence of unpaired electron leads to support the hydrogen bonding in it and its semiconductivity.

Since the structures of S_4N_4 and $S_4N_4H_4$ are reported as cyclic structure[10], the structure of TTADHF, being a derivative of S_4N_4, may be a cyclic structure, similar to S_4N_4 and $S_4N_4H_4$. Its geometrical array may be proposed as figure 1.

S. albus, *S. aureus* (gram-positive); *E. coli* and *P. pseudomonas* (gram-negative) bacteria were used during its antibacterial analysis and it is found that TTADHF is active to *S. albus*, *S. aureus* and *P. pseudomonas* despite its lack of effectiveness to *E. coli*. The activity of TTADHF to former three bacteria is in the following order.

S. albus (+3) > *S. aureus* (+2) > *P. pseudomonas* (+1).

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STUDIES ON AROYLMETHYLENE-SULPHONIUM YLIDES: SYNTHESIS OF SOME NEW 1,2,3-TRIARYLSUBSTITUTED CYCLOPROPANES VIA SULPHONIUM YLIDES

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THE use of sulphonium ylides in the synthesis of heterocycles[1] and cyclopropanation reactions[2,3] is documented. Utilizing this reaction with a view to exploring the synthetic potentialities of sulphonium ylides, we have studied the reactivity of these ylides (2a–c) towards α,β-unsaturated ketones (3a–f) and synthesized some new 1,2,3-trisubstituted cyclopropanes (4a–o).

Treatment of salts 1a–c with 10% aqueous sodium hydroxide generated an intense yellow colouration due to the formation of ylides (2a–c). The reactions of the ylides (2a–c) with α,β-unsaturated ketones (3a–f) at room temperature afforded trans- 1,2,3-trisubstituted cyclopropanes (4a–o). The exclusive formation of trans-1,2,3-trisubstituted cyclopropanes 4a–o suggested that the addition of the ylide to the ketone was due to the additional delocalization of charge over the conjugated system in the transition state. The trans-geometry of the cyclopropane derivatives 4a–r was determined on the basis of NMR spectra in which the three cyclopropyl protons exhibited as expected AB_2 pattern and the trans-coupling constants observed were in the range of 5 CPS to 6 CPS.

All the cyclopropanes (4a–o) synthesized are listed in table 1. The structures of the compounds 4a–o were determined on the basis of elemental analyses and IR and NMR spectral data.

Melting points were taken in a sulphuric acid bath and are uncorrected.

Phenacylidenedimethyl sulphurane (2a)

Phenacyldimethylsulphonium bromide (1a) (10 g) was dissolved in water (25 ml) and the coloured suspension was filtered. The clear filtrate was stirred with 10% aqueous sodium hydroxide (120 ml) for 3 hr and then extracted with $CHCl_3$, the $CHCl_3$ layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford 2a as orange solid (10 g), m.p. 55–56° (Lit[4] 56–57°).

3,4,5-*Trimethoxybenzylidene acetophenone* (3a)

A solution of sodium hydroxide (2 g in 10 ml of water) was added to a cooled solution of 3,4,5-trimethoxy benzaldehyde (9.8 g) and acetophenone (6 g) in ethanol (60 ml) dropwise. The reaction mixture was kept at 0–2° for 2.5 hr and left overnight in refrigerator. Water (150 ml) was added and the resulting precipitate was filtered. It was recrystallized from ethanol to give 4a (11.2 g, 75%), m.p. 144°; IR (nujol): 3000, 1665 (C=O), 1605 (C=C), 1230 and 1110 (OCH_3) and 820 cm^{-1}, PMR ($CDCl_3$; TMS): δ3.85 (*s*, 3H,OCH_3), 3.9 (*s*, 6H, 2-OCH_3), 6.5 (*d*, J = 8Hz, 1H, olefinic proton), 7–8.2 (*m*, 7H, Ar-H); (Found: C, 72.5; H, 6.2; $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.0%).

The following compounds were similarly prepared (m.p., yield %), 3b (117°, 75); 3c (108°, 76); 3d (125°, 78); 3e (154°, 73) and 3f (121°, 68).

1,2-*Dibenzoyl*-3-(3,4,5-*trimethoxyphenyl*)-*cyclopropane* (4a)

To a solution of 3a (2.98 g) in benzene (50 ml) was added 2a and the resulting solution was stirred for 15