

attributed to the proton of the dichloromethyl group at  $C_1$ . The NH proton was obtained as a broad singlet at 7.12  $\delta$ .

All the compounds gave satisfactory analysis for C, H and N.

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### SUBSTITUENT EFFECT OF THE $CF_3$ GROUP IN AROMATICS

THE effect of the  $CF_3$  group on the electron distribution of the phenyl part has been discussed by many workers<sup>1-6</sup>. Different mechanisms such as fluoride type no bond resonance, hyperconjugation and similar other mechanisms have been suggested to explain the strong electron withdrawing effect of the  $CF_3$  group.

Spectra of isomeric trifluorotoluidines  $CF_3C_2H_4NH_2$  have been studied in detail in solution as well as in the vapor phase. The solution spectra are shown in Fig. 1. On the basis of a large

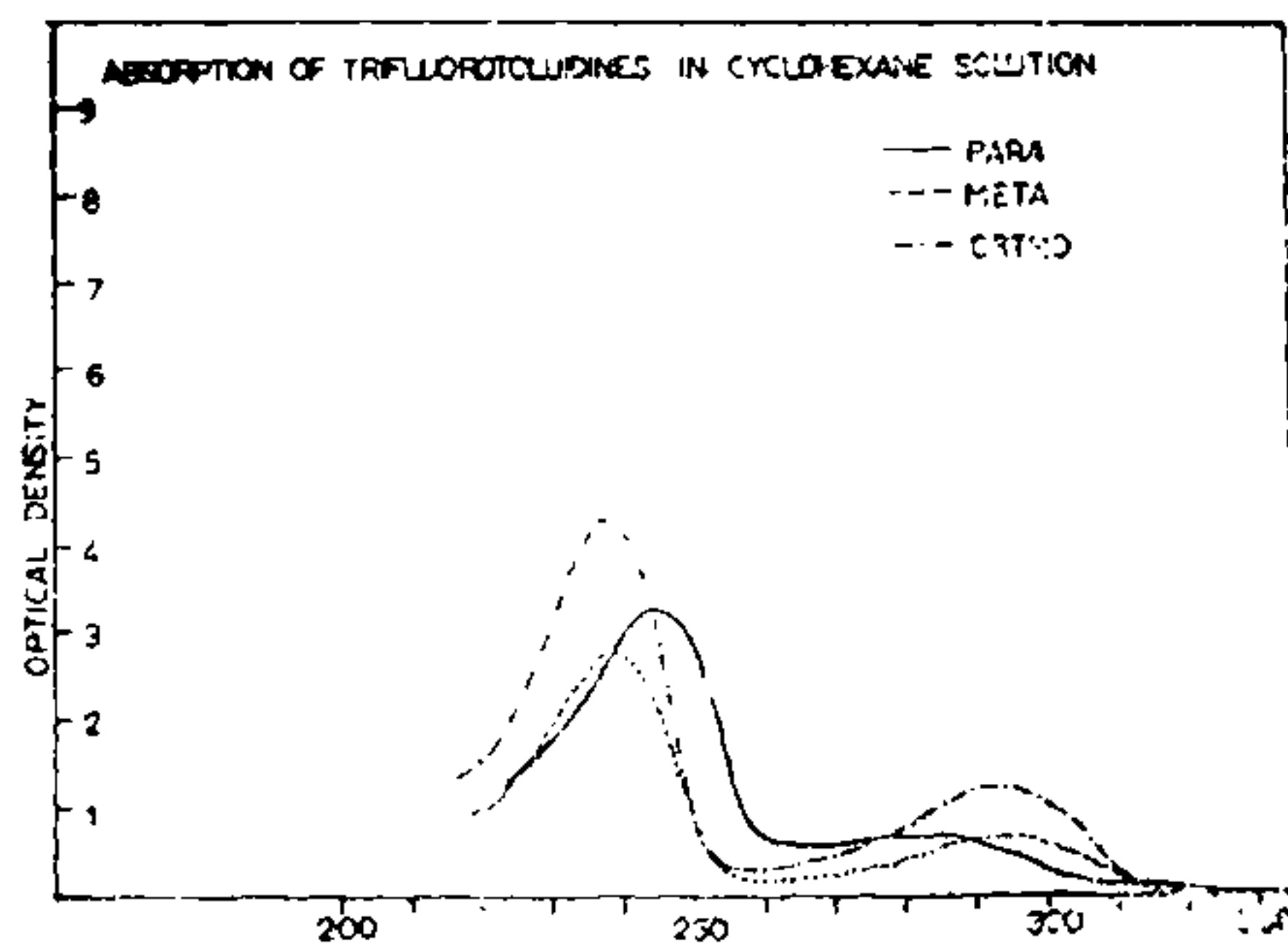


Fig. 1

amount of data on substituted anilines, Forbes and Leckie<sup>7</sup> have drawn some conclusions regarding the effect on the ultraviolet spectrum of aniline as a function of the nature of the substituent. Present results are discussed in the light of these as also general considerations of substituent effect.

The two bands generally observed in the spectra of substituted anilines in the region above 200  $m\mu$

are the usual B and C bands, the former being around 240  $m\mu$  and the latter around 295  $m\mu$ .

It has generally been accepted that the B band has a large contribution of intramolecular charge transfer state. The effect in para substituted anilines when the other substituent is an electron withdrawing, is a large bathochromic shift of the aniline B band and the C band remaining more or less in the same position. In some cases two bands merge giving only a broad single band. In the case of ortho and meta isomers, for acceptor substituents, quite often, two B bands are observed and the C band shows a large bathochromic shift.

In  $CF_3$  substituted anilines, since  $CF_3$  is an acceptor group, the spectral changes in general follow the above pattern, but there are some pertinent differences. First, the shift of the C band in meta and para isomers is much less than for other electron accepting substituents like formyl, acetyl with delocalised  $\pi$  orbitals. Secondly the B band does not show a splitting in ortho and meta isomers as in other cases. This shows that the electron withdrawal mechanism of  $CF_3$  group is different from the usual acceptors like formyl.

It is known that the spectral effects in case of unsaturated acceptors like formyl are principally due to  $\pi$  electron induction. Splitting of the B band in ortho and meta substitutions is due to the separation of the benzenoid B band and the aniline charge transfer band resulting from the pronounced lowering of the latter. The shift of the B band in para and of C in ortho and meta are also due to the some electronic effect. Thus the electron withdrawal mechanism of the  $CF_3$  group does not seem to be due to  $\pi$  induction but due to field effect. It is interesting to note that a similar idea has been put forward by Streitwieser and Holtz to account for the differences in reactivity.

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