The peak strength and position of the absorption bands are found to be correlated with the stability and association strength of the complexes. The results confirm concepts on the electron densities in the components.

The ionic complexes formed by the cations of triarylmethane dyes (TAMD) are widely used in analytic chemistry for isolation and determination of trace components. It has been shown [1, 2] that association occurs via the part of the cation bounded by the two most basic groups, the extreme structures having positive charges mainly localized there. The strength of the complex increases in proportion to the total positive charge on the association area, which itself is virtually equal to the sum of the charges on the end groups. The TAMD usually employed have the association area on the outside of the main conjugation chain of the cation [3-5]. The absorption spectra should therefore be related to the strength of association, since the basis of both is the electron distribution in the cations.

The specific charges on the end groups govern the donor action of these, such as the lability of the nonbonding p pair on the N in the diakylamino group; the strength of association increases with this action, as does the oscillator strength for the main absorption band. Hyperchromic and bathochromic shifts should also occur.

The only factor appreciably affecting the stability of the complex is the ionic interaction of the end groups with the anion, which is governed by the peripheral electron density of the anion, which thus directly affects the displacement of the nonbonding p pair and hence also the shift in the absorption band.

These arguments are correct if the end groups of the association area are the end groups of the main conjugation...
chain, and if reduction of the electron density at the end groups occurs only from redistribution of the electron density in that chain.

We have examined this for four groups of TAMD (A–D in Table 1). For the preparation and purification of I–VI see [6]; dye VII was made by the method of [7], while the synthesis of VIII–X is described in [8, 9]. The measurements were made with an SF-10 recording spectrophotometer.

Fig. 1. Absorption spectra in acetone-water (1:1) of: I) crystal violet; II) malachite green; III) brilliant green; IV) p,p'-bis-di-methylaminodiphenyl-3-carbazolyl methyl chloride; V) p,p'-bis-dimethylaminodiphenyl-3-(9-cyanoethyl)-carbazolylmethyl chloride.

The basicity of the dimethylamino groups as such does not vary in series I, IV, and II. Reduced competition from \( R'' \), whose basicity decreases in that order, leads to more pronounced localization of positive charge on \( R' \) and \( R'' \). The position is even more favorable to localization on the diethylamino groups of III. The chlorides of I, IV, II, and III show hyperchromic and bathochromic shifts in the main absorption band (Fig. 1a), and this is also the sequence of increasing strength of association with complex anions [2]. For IV and V it is difficult to compare the charges on the association ar-

\*The main band of I coincides with nearly equivalent bands due to the two other conjugation chains, and the hyperchror shift is a resultant effect.