TWO FORMS OF COMPLEXES OF HETEROONIUM
# SALTS WITH AMINES

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Heteroonium salts form molecular compounds of two forms with amines: true π complexes (charge-transfer complexes) and complexes with a localized σ bond between the components.

The complex nature of the deep coloration [2] of mixtures of heteroonium (quinolinium, acridinium, and benzacridinium) salts with aromatic amines was shown in [1]. The resulting molecular compounds were classified as π complexes with a mesomeric (resonance) structure [in modern terminology, charge-transfer complexes (CTC)], a characteristic feature of which is the dependence of their absorption bands on the ionization potentials of the donors and the electron affinities of the acceptors [3]. Moreover, it was found [1] that the absorption spectra of the complexes are independent of the onium acceptor components (AC) when p-dimethylaminostyryl derivatives of quinoline or acridine are used as the donor components (DC).

We have studied the absorption spectra of complexes using the onium salts of nitrogen-, sulfur-, and oxygen-containing heterocycles — 1-ethylquinolinium (I), 10-methylacridinium (II), thioxanthylium (III), and xanthylium (IV) perchlorates* — as the acceptors, with allowance for the fact that the acceptor properties of the onium salts increase successively as the area of the π system increases [3] and also when the nitrogen heteroatom is replaced by S and O in a series of related heteroonium cations (II-IV).

I, λ_{max} 320 nm   II, λ_{max} 422 nm   III, λ_{max} 515 nm   IV, λ_{max} 435 nm
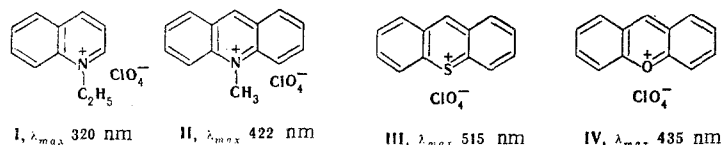
Aromatic amines (for example, dimethylaniline and p-dimethylaminoacetanilide) and amines containing a quinoline or acridine ring [for example, 2-(p-dimethylaminostyryl)quinoline (V, λ_{max} 392 nm) and 9-(p-dimethylaminostyryl)acridine (VI, λ_{max} 430 nm) in the trans forms] were tested as donor components.

All of the spectra were obtained from solutions in dry dichloroethane, in which both components are stable. The complexes were obtained by mixing of separately prepared solutions of the components at room temperature.

According to the concept of the formation of a CTC, the maximum of the absorption band should be shifted bathochromically as the electrophilic properties of the onium cation increase. This shift is actually observed in complexes of onium salts with aromatic amines that do not contain quinoline or acridine rings. Thus the bathochromic shift of the maximum of the complex is 130 nm on passing from quinolinium salt I to acridinium salt II: λ_{max} with dimethylaniline is, respectively, 430 and 560 nm, as compared with 500

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* Perchlorates have an advantage over halides, since their absorption spectra, in contrast to the spectra of the halides [4], obey the Lambert—Beer law. This will lead to stabilization of the position of the maximum in the spectrum of the complex. The problem will be examined in detail in a special communication.

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and 630 nm with p-dimethylaminoacetanilide. Consequently, the complexes of salts I-IV with these amines must be classified as true π complexes with a delocalized bond between the components (CTC); this is also confirmed by the determination of the constants [5].

A new broad band that indicates the formation of an associate is also observed in the visible region in the spectra of solutions of salts I-IV with amines that contain a quinoline (V) or acridine (VI) ring. However, the position of the maximum does not change when the onium salt is replaced: the λ_{max} values of solutions of all of the onium salts of I-IV with a single amine coincide completely. Thus the complexes of 2-(p-dimethylaminostyryl)quinoline (V) with acceptors I-IV have λ_{max} 525 nm, and the solutions are crimson-colored; the complexes of 9-(p-dimethylaminostyryl)acridine (VI) have λ_{max} 612 nm, and the solutions are blue. The identical character of the spectra in the long-wave region and the dependence of the position of the absorption bands only on the donor components cannot be explained by the concept of complex mesomerism or intermolecular charge transfer. The reason must be sought in the possibility of the formation in the associates of chromophoric structures from the donor components (DC), which would correspond to absorption in the visible region of the spectrum.

Nitrogen heterocycles of the quinoline type, which have an unshared pair of electrons attached to the nitrogen atom (nucleophiles),coordinately add Lewis acids (electrophiles) to give σ complexes [6].

Complexes of onium salts I-IV with bases of the V and VI type can be similarly represented as products of the addition of onium cations (electrophiles) to the unshared pairs of the electrons of the nitrogen atoms of the heterorings of donor systems V and VI. The onium cations can be added coordinately in the form of carbonium structures, for example, IIb, with the formation of localized σ bonds, i.e., with the formation of σ complexes (VII, for example).*

If the concept proposed by us is correct, the chromophore system of the donor component in the complex should be transformed into the cation structure with the conjugated system of a cyanine dye and should be blue. The long-wave band in the spectrum should be the absorption band of the conjugated cation (halochromic salt VII) rather than the band of charge transfer from the donor component to the acceptor components [7];

VI, DC

a III, AC b
DC

VII, λ_{max} 612 nm
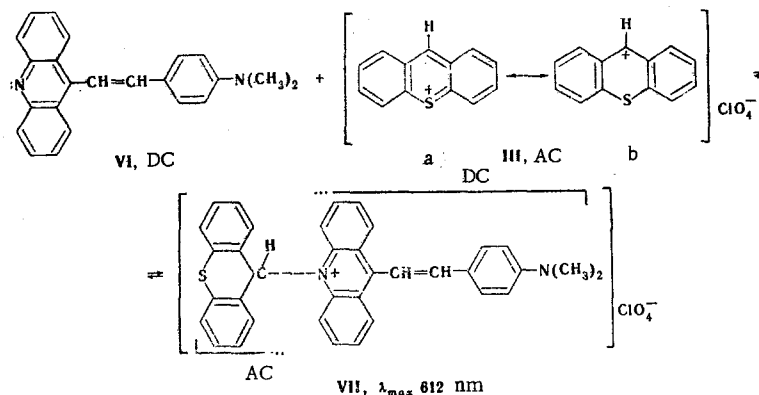
it should depend only on the structure of the donor component; this is also confirmed by a study of the spectra. The conclusion regarding the formation of a localized σ bond as a result of coordinate addition of heteroonium salts to the amines is confirmed by an additional experiment, namely, that the hemicyanine dyes obtained by condensation of p-dimethylaminobenzaldehyde with 2-methylquinolinium salts [1] or 9-methylacridinium salts have a color and an absorption band that coincide with the color and absorption band of the molecular compounds described. We explain the identical character of the spectra of complex VII and dye VIII in the long-wave region by the identical character of the chromophore structures of the cations.

VIII, λ_{max} 616 nm

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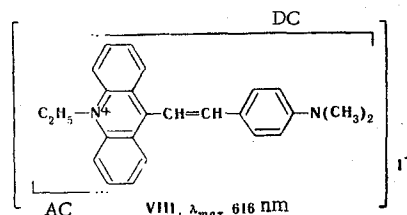
*In view of the high lability of the σ bond in adduct VII, it is depicted by a dash line.
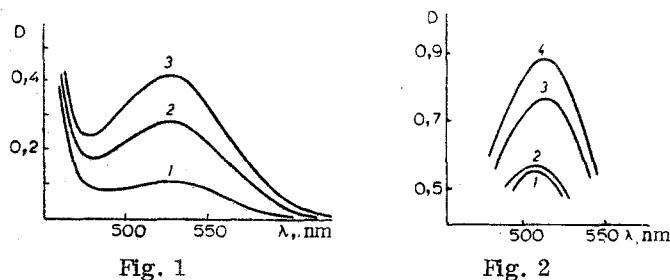
Fig. 1   Fig. 2

Fig. 1. Change in the optical density of complex (II + V): 1) 4
min after preparation; 2) after 7 min; 3) after 12 min.

Fig. 2. Absorption spectra of solutions of melts of IX and X in
the presence of amine V: 1) N-methylacridinium iodide + V;
2) IX (Y = NCH$_3$) + V; 3) X (Y = S) + V; 4) X (Y = O) + V.

In addition, the spectra of the molecular compounds (AC + DC) in the long-wave region are identical
to the spectra of amines V and VI in solutions in protic acids. Consequently, a similar chromophore sys-
tem of a conjugated cation (complex of the addition of a proton, VIII, AC = H, λ_{max} 614 nm) is formed in
the protonation of the nitrogen atom of the heteroring.

In this case, the complexes of heteroonium salts with amines that contain a quinoline or acridine ring
do not have paramagnetic properties. Finally, the complex-free components equilibrium is not set up in-
stantaneously but gradually in the course of several hours (Fig. 1). It is due to the ease of heterolytic cleav-
age of the strongly polarized σ bond in the associate between the tetrahedral carbon atom and the nitrogen
atom in the cationic immonium structure. In confirmation, one can adduce the presence (as established by
us) of extremely labile σ bonds in typical covalent compounds (for example, IX and X), which contain xanthyl,
thioxanthyl, and 9,10-dihydroacridyl radicals.

In the crystalline state, IX and X are colorless substances that absorb at up to 320 nm. However, their
melts have the color of the corresponding cations of II-IV: yellow when Y = NCH$_3$, and red when Y = O, S.
Solutions of the melts initially also have a visible color, but they are rapidly decolorized on standing. These
observations attest to dissociation of IX and X into ions at the C−S or C−C bonds during melting and asso-
ciation of the ions into covalent compounds in solutions. In view of the rapid transition in solutions of the
ionic (colored) forms into covalent (uncolored) forms, it is difficult to record the spectra of the colored
forms. We therefore stabilized the cationic onium structures by the addition of amines V and VI and identi-
fied them in the form of complexes (AC + DC). Melts of IX and X that contain heteroonium cations give the
absorption bands characteristic for complexes of salts I-IV (Fig. 2) with amines V and VI.

IX   X

Y = O, S, NCH$_3$
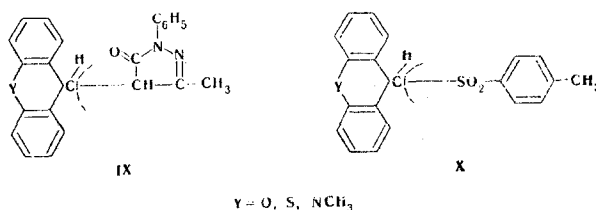
Especially high bond lability is observed for 1-phenyl-3-methyl-4-(10-methyl-9,10-dihydro-9-acridyl)-
5-pyrazolone (IX, Y = N−C H$_3$). Heterolytic cleavage of the bond between C-9 of the acridine portion of the
molecule and C-4 of the pyrazolone ring is observed when this compound is dissolved in ethanol, acetone,
nitrobenzene, and other polar solvents at room temperature. These observations are in agreement with in-
vestigations of the products of condensation of aminotriarylcarbinols with 1-phenyl-3-methyl-5-pyrazolone,
which in polar solvents exist as an equilibrium mixture of dissociated and undissociated forms [8].

Because of the presence of labile bonds, IX and X are extremely reactive and can be used as inter-
mediates in synthesis, for example, in alkylation [9].

It is also very important to note that the addition of absolute alcohol to solutions of complexes with
onium salts III and IV in dichloroethane leads to the disappearance of the color of the complex and reduc-
tion of the color of the amines. With alcohol the onium acceptor components give uncolored alcoholysis and

disproportionation products and $HClO_4$ [10]. Amines V and VI are stable in alcohol solution. However, the resulting acid proves to be inadequate for the formation of a cation of the VIII type. Consequently, the color in solutions of V and I-IV and also VI and I-IV is not a consequence of hydrolysis and transition of amines V and VI to a complex by addition of a proton.

EXPERIMENTAL

1-Phenyl-3-methyl-4-thioxanthyl-5-pyrazolone (IX, Y = S). A mixture of 1.07 g (5 mmole) of thioxanthydrol and 1.3 g (7 mmole) of 1-phenyl-3-methyl-5-pyrazolone in 20 ml of methanol was refluxed for 20 min, after which it was cooled, and the precipitate was removed by filtration and washed with alcohol to give 1.7 g (90%) of colorless crystals with mp 182° (from alcohol). Found: N 7.6; 7.5%. $C_{23}H_{18}N_2OS$. Calculated: N 7.6%.

1-Phenyl-3-methyl-4-xanthyl-5-pyrazolone (IX, Y = O). This compound was obtained as colorless plates with mp 210-212° (from alcohol). Found: N 8.1; 8.1%. $C_{23}H_{18}N_2O$. Calculated: N 7.9%.

1-Phenyl-3-methyl-4-(10-methyl-9,10-dihydro-9-acridyl)-5-pyrazolone (IX, Y = N—CH_3). A mixture of 1.5 g (7 mmole) of 10-methyl-9-methoxy-9,10-dihydroacridine [11] and 2 g (12 mmole) of 1-phenyl-3-methyl-5-pyrazolone in 10 ml of methanol was stirred at room temperature for 30 min. The precipitate was removed by filtration to give 1.85 g (72%) of product. It was purified by two precipitations from acetone solution by the addition of water acidified with acetic acid to give a gray substance with mp 166°. IR spectrum: $\nu_{C=O}$ 1640 cm^{-1}. Found: N 11.7; 11.8%. $C_{24}H_{21}N_3O$. Calculated: N 11.2%.

p-Tolyl Xanthyl Sulfone (X, Y = O). A solution of 1.6 g (0.01 mole) of p-toluenesulfinic acid in 5 ml of alcohol was added with stirring to a warm solution of 2 g (0.01 mole) of xanthydrol in 5 ml of alcohol. The mixture was then stirred for 30 min, and the precipitate was removed by filtration and washed with water to give 2.6 g (70%) of colorless plates with mp 215-216° (from alcohol) [12]. IR spectrum: 1130-1140 and 1320 cm^{-1} (sulfonyl group).

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