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X-Ray Study of 1,4-Dianilidoanthraquinone and 1,4-Dimesidinoanthraquinone

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The sulfonic acids of 1,4-di-(arylamino)-anthraquinone constitute an important group of fast dyes for wool. Most 1,4-di-(arylamino)-substituted anthraquinones are green in color; the exceptions are derivatives in which all the ortho-position hydrogen atoms of the aryl residues have been replaced. Such compounds, as well as the corresponding alkylamino and hydroarylamino derivatives, have an intense bright-blue color.

Measurement of the light absorption of solutions of 1,4-di-(arylamino)-anthraquinones in CCl_4 in the visible and ultraviolet regions of the spectrum showed that, in the presence of methyl or ethyl groups or bromine atoms in all ortho positions of the phenyl residues, or in the 2,3 positions of anthraquinone, absorption is absent in the short-wavelength part of the spectrum, and the principal maximum is shifted toward shorter wavelengths ([1]). In view of the fact that the substituents listed obviously preclude the placement of the phenyl residues in the plane of the main part of the molecule, it was logical to regard the appearance of an additional absorption band and the deepening of the main one in the absence of steric hindrance as a consequence of coplanarity of the molecule. A comparison of absorption frequencies in the infrared part of the spectrum also supports this assumption ([2]).

	λ(N—H), cm^{-1}	λ(C=O), cm^{-1}
1,4-di-(*p*-tolylamino)-anthraquinone	3120	1620
1,4-di-(mesitylamino)-anthraquinone	3175	1630
1,4-di-(*p*-tolylamino)-2,3-dimesityl-anthraquinone	3230	1640

The data presented indicate a weakening of the intramolecular hydrogen bond between the carbonyl oxygen and the hydrogen of the amino groups when steric obstacles to the coplanar arrangement of the benzene nuclei are present. This weakening of the bond is the result of an increase in the distance due to the displacement of hydrogen from the plane of the anthraquinone rings and is caused by disruption of the conjugation system ([3]).

For the compounds under consideration, the force holding the phenyl residues in the plane must be recognized as the π-electron interaction of the nitrogen atoms with the aromatic nuclei bound to them ([4,5]). Since the presence of such interaction is of substantial importance for understanding the chemistry and color not only of a large number of practically important arylamino derivatives of anthraquinone, but also of many other secondary aromatic amines, it was desirable to find direct proof of the planar structure of molecules of 1,4-di-(arylamino)-anthraquinone derivatives in the absence of steric hindrance.

To resolve the question of the coplanarity of the benzene rings with the plane of the main part of the molecule, X-ray measurements were carried out on crystals of two compounds:

[structural formulas of compounds I and II]

I II

1,4-dianilidoanthraquinone (I) and **1,4-dimesididoanthraquinone (II)**. In the free molecule of compound I, steric hindrance between the CH groups of the anthraquinone and benzene rings is possible, forcing the latter to rotate by an angle of about 20° relative to the plane of the main part of the molecule (if the valence angle C—N—C is taken to be straight). In the free molecule of compound II, the presence of CH_3 groups attached to the benzene ring forces it to rotate by an angle of not less than 60° relative to the plane of the anthraquinone ring.

Table 1

Compound	a, Å	b, Å	c, Å	β	Pycnometric density	X-ray density	Number of molecules	Space group
1,4-dianilidoanthraquinone (I)	12.2	8.73	17.8	108°	1.51	1.52	4	$C_{2h}^5 = P2_1/c$
1,4-dimesididoanthraquinone (II)	7.98	19.8	17.2	103°	1.20	1.28	4	$C_{2h}^5 = P2_1/c$

Table 1 gives the results of X-ray measurements of the unit cells, space groups, and densities of the above-mentioned compounds. On the basis of consideration

Fig. 2. Arrangement of molecules of 1,4-dimesididoanthraquinone in projection onto the *bc* plane. Solid lines—molecules of one layer; dotted lines—of another layer (not all molecules in the cell are shown).

Figure 1: Fig. 2. Arrangement of molecules of 1,4-dimesididoanthraquinone in projection onto the *bc* plane. Solid lines—molecules of one layer; dotted lines—of another layer (not all molecules in the cell are shown).

of the unit-cell dimensions of compound I, it may be assumed that the main part of the molecule of this compound is parallel or nearly parallel to the plane *ac*, since the *b* axis is the shortest (8.73 Å). From the symmetry conditions of the space group $C_{2h}^5 = P2_1/c$, it follows that perpendicular to the *b* axis there passes a plane—

[crystal packing diagram]

Fig. 1. Arrangement of molecules of 1,4-dianilidoanthraquinone in projection onto the *ac* plane (only one layer of molecules is shown)

⋯a glide plane with a shift along the *c* axis, as a result of which, with 4 molecules in the unit cell, they are arranged in layers perpendicular to the *b* axis. A variant of such an arrangement is shown in Fig. 1. This arrangement permits a slight rotation of the benzene nucleus relative to the rest of the molecule, and also some possible rotation of the entire molecule relative to the *ac* plane. Consequently, the packing of molecules in the crystal does not require any additional change in the angle of rotation of the benzene nucleus as compared with the free molecule.

The shortest axis in the crystal of compound II is the *a* axis (7.98 Å). Its length almost coincides with the dimensions of the benzene nucleus and the CH_3 groups attached to it (8.8 Å). Dense packing of molecules in the crystal and fulfillment of the symmetry conditions of the space group for molecules of compound II can occur with the arrangement of the molecules as shown in Fig. 2. As can be seen, in this variant of the arrangement the benzene nuclei are rotated through an angle equal to or close to 90° relative to the main part of the molecule.

The benzene nuclei of neighboring molecules, as it were, hook onto one another, producing dense packing. Arrangement of the molecules without the indicated interlocking of the benzene nuclei is not allowed by the established dimensions of the unit cell. As a consequence of such an arrangement of the molecules in the crystal of compound II, the possibility of torsional vibrations of the attached benzene nuclei is practically excluded.

Fig. 2. Arrangement of molecules of 1,4-dimesididoanthraquinone in projection onto the *bc* plane. Solid lines—molecules of one layer; dotted lines—of another layer (not all molecules in the cell are shown).

In the absence of steric hindrances, as is the case in the molecule of, for example, 1,4-dianilidoanthraquinone, the attached benzene nuclei remain almost coplanar with the main part of the molecule, as shown by the X-ray study of crystals of this compound. In this case, as was assumed above, the π-electron interaction of the nitrogen atoms with the aromatic nucleus retains its substantial significance.

The attachment of methyl groups in all meta positions to the benzene ring creates such considerable steric difficulties in the molecules that, as the X-ray study of the crystal of 1,4-dimesididoanthraquinone has shown, the departure from coplanarity with the anthraquinone rings is close to 90°. The consequence of this, as spectroscopic data show, is a significant weakening of the intramolecular bond.

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Note: Figure translations are in progress. See original paper for figures.