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Abstract

Full Text

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ON COLOR PHENOMENA IN DIACYL DERIVATIVES OF *p*-AMINOPHENOL

(Presented by Academician B. A. Kazanskii, January 22, 1958)

In previous communications (^{1}) we showed that, when two different electron-donor systems* (AK and A′K) are present in a compound simultaneously with an electrophilic system** (BK) that is not connected with the former by a chain of conjugated double bonds, this compound can sometimes be obtained in the form of two differently colored modifications. The existence of the latter was explained by the fact that the direct interaction of the electrophilic and electron-donor systems by means of exomolecular forces (^{2}), which is the principal factor responsible for the color of "compounds with separate chromophoric systems," *** can in this case occur in two ways: either the electrophilic system interacts with the electron-donor system AK, or with the system A′K.

In the present communication compounds constructed according to types I and II are considered. In these compounds the electrophilic system (BK) is the acyl of 4-nitrobenzoic or 3,5-dinitrobenzoic acid (RCO), the electron-donor system AK is the molecule of *p*-aminophenol (diacylated), and the electron-donor system A′K is the acyl of trimethylgallic acid (R′CO).

$$\text{I}\quad \underset{\text{BK}}{\text{RCONH}}-\underset{\text{AK}}{\text{C}_6\text{H}_4}-\underset{\text{A}'\text{K}}{\text{OCOR}'}\qquad \text{II}\quad \underset{\text{BK}}{\text{RCOO}}-\underset{\text{AK}}{\text{C}_6\text{H}_4}-\underset{\text{A}'\text{K}}{\text{NHCOR}'}$$

From Table 1 it can be seen that almost all diacyl derivatives of *p*-aminophenol (with the exception of No. 2) containing the system A′K form two colored modifications: a weakly colored pale-yellow modification (a) and a more deeply colored yellow modification (b). Both modifications can be transformed into one another by crystallization from different solvents (see the experimental part), and sometimes this transformation takes place quite visibly. Thus, for example, the pale-yellow modification of compound (No. 4) isolated from acetone becomes noticeably more yellow even upon simple treatment with alcohol; the pale-yellow modification of compound (No. 6) begins to turn yellow while still in the mother acetone solution. In compounds not containing the electron-donor system A′K, it was not possible in a single case to obtain two differently colored modifications. Hence one may conclude that the possibility of existence of the compounds under consideration in the form of a more deeply colored modification is associated with the presence in them of the system A′K. This system contains three OCH_3 groups, the electron-donor action of which is weakened by the presence in it of the CO group. But since the electrophilic action of the latter is in sig- to a considerable extent suppressed by the NH- or OH-group attached to it, then its influence on the electron-donor properties of the system A′K must be small. Therefore one may consider that the system A′K is a stronger electron-donor system than AK, since in the latter the donor properties of both the amino and the hydroxy group are suppressed to a considerable degree by the CO groups attached to them. It is further necessary to bear in mind that the system A′K is not conjugated with the system BK, and therefore the interaction of these systems, which accounts for the deeper color of form (b), can occur only by means of exomolecular forces.

The presence of color, albeit weaker, in compounds having only one electron-donor system AK indicates that the system BK can also interact with the system AK. In compounds of type I this possibility is all the more probable because

Table 1

Color of diacyl derivatives of *n*-aminophenol

No.	Formula of the compound	Color of the substance in crystals, form (a)	Color of the substance in crystals, form (b)
1	$O_2N-C_6H_4-CONH-C_6H_4-OCO-C_6H_5$	greenish	
2	$O_2N-C_6H_4-CONH-C_6H_4-OCO-C_6H_2(OCH_3)_3$	slightly greenish	
3	$(O_2N)_2C_6H_3-CONH-C_6H_4-OCO-C_6H_5$	pale yellow	
4	$(O_2N)_2C_6H_3-CONH-C_6H_4-OCO-C_6H_2(OCH_3)_3$	»	bright yellow
5	$O_2N-C_6H_4-COO-C_6H_4-NHCO-C_6H_5$	greenish-yellow	
6	$O_2N-C_6H_4-COO-C_6H_4-NHCO-C_6H_2(OCH_3)_3$	pale yellow	bright yellow
7	$(O_2N)_2C_6H_3-COO-C_6H_4-NHCO-C_6H_5$	greenish-yellowish	
8	$(O_2N)_2C_6H_3-COO-C_6H_4-NHCO-C_6H_2(OCH_3)_3$	pale yellow	yellow

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* An electron-donor system is a conjugated chain of double bonds with an electron-donor group attached to it (NH_2, OH, etc.).

** A conjugated chain of double bonds with an electrophilic group attached to it (CO, NO_2, etc.).

*** In other words, compounds in which the electrophilic and electron-donor systems are not connected with one another by conjugated double bonds.

here this interaction can occur not only by means of exomolecular forces but, to some extent, also along the chain of conjugated double bonds formed as a result of tautomerization of the CONH group (^{3}). The similarity of the color of compounds having one electron-donor system (AK) to the color of compounds having both electron-donor systems gives grounds to consider that the color

the lightly colored form of the latter is also conditioned by the interaction between the BK and AK systems, while the interaction between BK and A′K is disrupted.

It is further interesting to note that in almost all cases the lightly colored forms of compounds containing the benzoyl acidyl are colored somewhat more deeply than the corresponding compounds containing the trimethylgallic acidyl; this is especially noticeable in compounds of type II.

A comparison of the coloration of compounds of types I and II shows that the latter, as a rule, are colored somewhat more deeply than the former. An explanation for this can be found by proceeding from an analysis of the relative “strength” of the interacting systems in the one case and in the other. The BK system is stronger in compounds of type I, because the OH group weakens the electrophilic properties of the CO group to a lesser degree than the amino group. For the same reason, the A′K system also proves stronger in compounds of type II. The AK systems of compounds of types I and II do not differ substantially in strength.

Experimental Part

N-[4-nitrobenzoyl]-O-benzoyl-*p*-aminophenol (Table 1, No. 1). A mixture of N-[4-nitrobenzoyl]-*p*-aminophenol (4) (1 mole) and benzoyl chloride (4 moles), dissolved in nitrobenzene, was heated for half an hour almost to boiling. The reaction product was recrystallized from pyridine. Greenish scaly crystals with m.p. 276–277°, sparingly soluble in ordinary organic solvents, comparatively readily soluble in pyridine.

Found %: N 7.77
$C_{20}H_{14}O_5N_2$. Calculated %: N 7.76

N-[4-nitrobenzoyl]-O-[3,4,5-trimethoxybenzoyl]-*p*-aminophenol (Table 1, No. 2).

Prepared as the preceding compound. Recrystallized from pyridine, and then from a mixture of pyridine and methanol (1 : 1). Slightly greenish crystals with m.p. 246–247°, fairly readily soluble in pyridine, less readily in acetone and dichloroethane, sparingly in alcohol.

Found %: N 6.15
$C_{23}H_{20}O_8N_2$. Calculated %: N 6.20

N-[3,5-dinitrobenzoyl]-O-benzoyl-*p*-aminophenol (Table 1, No. 3). Prepared from N-[3,5-dinitrobenzoyl]-*p*-aminophenol (5) and benzoyl chloride by the Schotten–Baumann reaction. Recrystallized from acetone and then from alcohol. Long, narrow plates of pale-yellow color with m.p. 226–226.5°, fairly readily soluble in acetone, less readily in alcohol and benzene.

Found %: N 10.43
$C_{20}H_{13}O_7N_3$. Calculated %: N 10.32

N-[3,5-dinitrobenzoyl]-O-[3,4,5-trimethoxybenzoyl]-*p*-aminophenol (Table 1, No. 4). This and the following preparations were obtained analogously to the preceding compound. Recrystallized twice from acetone. Pale-yellow prismatic crystals with m.p. 218–219°. On treatment with alcohol the preparation turns yellow and is isolated from the alcoholic solution in the form of a bright-yellow-colored form with the same melting temperature. The yellow form is isolated very well from dichloroethane—in the form of rhombic crystals. On recrystallization from acetone or toluene the yellow form is again converted into the pale-yellow one. The latter turns yellow on storage. Both forms are readily soluble in acetone and dichloroethane, fairly readily soluble in toluene, and less readily in alcohol.

Form (a). Found %: N 8.48
$C_{23}H_{19}O_{10}N_3$. Calculated %: N 8.45

Form (b). Found %: N 8.37
$C_{23}H_{19}O_{10}N_3$. Calculated %: N 8.45

N-Benzoyl-O-[4-nitrobenzoyl]-*p*-aminophenol (Table 1, No. 5). Starting substances: N-benzoyl-*p*-aminophenol and *p*-nitrobenzoyl chloride. Recrystallized twice from pyridine. Greenish-yellow crystals with m.p. 285—286°, sparingly soluble in ordinary organic solvents, comparatively readily soluble in pyridine.

Found, %: N 7.75
$C_{20}H_{14}O_5N_2$. Calculated, %: N 7.76

N-[3,4,5-Trimethoxybenzoyl]-O-[4-nitrobenzoyl]-*p*-aminophenol (Table 1, No. 6). Starting substances: N-trimethoxybenzoyl-*p*-aminophenol and *p*-nitrobenzoyl chloride. Recrystallized from acetone and then from alcohol. Bright-yellow crystals with m.p. 218.5—219.5°. From dichloroethane, and still better from a mixture of dichloroethane with benzene, a pale-yellow form separates in the form of fine-fibrous crystals with the same melting point.

Form (a). Found, %: N 6.28
$C_{23}H_{20}O_8N_2$. Calculated, %: N 6.20
Form (b). Found, %: N 6.34
$C_{23}H_{20}O_8N_2$. Calculated, %: N 6.20

N-Benzoyl-O-[3,5-dinitrobenzoyl]-*p*-aminophenol (Table 1, No. 7). Starting substances: N-benzoyl-*p*-aminophenol and 3,5-dinitrobenzoyl chloride. Recrystallized from acetone. Greenish-yellow plates with m.p. 222–223°, readily soluble in pyridine, fairly readily in acetone, less readily in dichloroethane and toluene, sparingly in alcohol.

Found, %: N 10.39
$C_{20}H_{13}O_7N_3$. Calculated, %: N 10.32

N-[3,4,5-Trimethoxybenzoyl]-O-[3,5-dinitrobenzoyl]-*p*-aminophenol (Table 1, No. 8). Starting substances: N-trimethoxybenzoyl-*p*-aminophenol and 3,5-dinitrobenzoyl chloride. Part of the product was recrystallized from acetone, another part from alcohol and then from dichloroethane. From acetone a yellow form separated with m.p. 211–211.5°; from dichloroethane, a pale-yellow form, in the form of silky crystals, with the same melting point. On crystallization from dichloroethane it is necessary to add the corresponding seed crystals (pale-yellow), otherwise a mixture of both forms separates, sometimes only the yellow form. The latter is well obtained from acetic acid. Both forms are fairly readily soluble in dichloroethane and acetone, less readily in toluene and alcohol.

Form (a). Found, %: N 8.53
$C_{23}H_{19}O_{10}N_3$. Calculated, %: N 8.45

Form (b). Found, %: N 8.47
$C_{23}H_{19}O_{10}N_3$. Calculated, %: N 8.45

N-[3,4,5-Trimethoxybenzoyl]-*p*-aminophenol. Obtained analogously to the nitrobenzoyl derivatives of *p*-aminophenol ([5]). Recrystallized twice from dilute alcohol. Rhombic crystals with m.p. 231.5–232.5°, readily soluble in acetone, alcohol, and benzene, considerably less readily in water.

Found, %: N 4.79
$C_{16}H_{17}O_5N$. Calculated, %: N 4.62

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