COMPLEXING OF SOME HETEROCYCLIC ANALOGS OF DIPHENYLPICRYLHYDRAZINE WITH AMINES

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The complexing of α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-picrylhydrazine and α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazine with ammonia and trimethylamine in both the solid state and in solvents (benzene, acetone, hexafluorobenzene, and heptane) was investigated. It was demonstrated that complexing does not depend on the donor and acceptor characteristics of the molecules but is determined by the structural peculiarities of the substance in solution and in the crystalline state.

In the present paper, we investigated α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-picrylhydrazine (I) [1] and α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazine (II) [2].

It has been previously shown [3] in the case of complexes of diarylpicrylhydrazine with amines that the structure of the solid-phase state, which also determines the chemical and physical properties of the substance in condensed phases, may be retained in solution. We have also noted [1] the interesting fact of the disappearance of paramagnetism and the characteristic absorption maximum in the visible region on the addition of I to a solution of 6-methylbenzothiazolylphenylpicrylhydrazyl, which is inexplicable from the point of view of the molecular structure of the solution. However, this phenomenon finds an explanation if the properties of I and the radical mentioned above are considered to be a function of the macromolecular structures of these compounds. Since cases of such anomalous behavior of radicals are frequent for heterocyclic analogs of diphenylpicrylhydrazine (DPPH) [4], we also investigated the complexing of hydrazines I and II with ammonia and trimethylamine in the solid state and in a number of solvents (benzene, acetone, hexafluorobenzene, and heptane).

When $N(CH_3)_3$ is bubbled through crystalline I, the latter forms a black complex (III), which is extremely stable in air and does not decompose even under high vacuum and on heating to 100°C. The same hydrazine reacts with ammonia to give a brown complex (IV) that decomposes rapidly in air. Hydrazine II in the solid state does not form a complex with either trimethylamine or ammonia.

Considering that the removal of a nitro group on passing from I to II substantially reduces the acceptor properties of the latter, it might have been assumed that complexing is a selective process that depends on the donor and acceptor characteristics of the reaction components.

In this case, a similar pattern should have been observed in solutions. However, when NH_3 was bubbled through a solution of I, we observed a change in color but were unable to isolate a crystalline complex, while hydrazine II in acetone gives an almost black crystalline complex (V) with NH_3 that is stable in the presence of a solvent.

As for the reaction of I and II with $N(CH_3)_3$, II in solution and in the solid state remains inert with respect to trimethylamine.

A solution of I in benzene turns red when the amine is bubbled through it. The addition of heptane to this red solution precipitates red crystals of a 1 : 2 complex (VI) of I with $N(CH_3)_3$ that are stable on heating

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to 100° under high vacuum. A black complex that was identical to III was obtained from the benzene solution on more prolonged passage of the amine. It has the 1 : 3 composition. The same complex is formed when the amine is bubbled through a saturated benzene solution of I. However, a solution of I in hexafluorobenzene gives only complex VI no matter how long it is treated with $N(CH_3)_3$.

Complex VI could not be converted to III by bubbling amine through crystalline VI. However, if $N(CH_3)_3$ is bubbled through a suspension of VI in heptane, it is gradually converted to III, i.e., the color and composition change.

The fact that hydrazine II, which has a poorer (as compared with picryl) 2,6-dinitrophenyl acceptor grouping, forms a complex with NH_3 in solution, while I does not form one, and the fact that II does not form a complex with the better donor $N(CH_3)_3$ but does form a complex with NH_3, provides a basis to assume that complexing is independent of the donor and acceptor characteristics of the molecules participating in it and is in all likelihood unselective.

In addition, the stability of complex VI in the crystalline state on prolonged passage of $N(CH_3)_3$ indicates that the difference between VI and III does not reside simply in the different amounts of added amine molecules.

The determining factors for complexing are probably the structural peculiarities of the substances in solution and in the crystalline state, as has been demonstrated in [3].

In this case, both benzene and heptane, saturated with $N(CH_3)_3$, can be considered to be "active" solvents that change the geometry of the complex and facilitate conversion of VI to III.

EXPERIMENTAL

The investigated hydrazines (I [1] and II [2]) were purified and vacuum-dried to remove the crystallization solvent.

The formation of complexes was monitored visually from the change in the color of the solution or the solid.

The amines were purified by passing them through a bottle filled with crystalline NaOH and a solvent identical to that used in the experiment, after which they were passed through glass tubes filled with the crystalline hydrazine or into test tubes containing solutions of I and II. The amine flow rate was monitored with a flow meter.

Complex III. This almost black crystalline product had mp 120-122° (dec.). Found: C 54.22; H 6.11; N 19.79%. $C_{20}H_{14}N_6O_6S \cdot 3C_3H_9N$. Calculated: C 54.12; H 6.39; N 19.60%.

Complex VI. This complex was obtained as red plates with mp 128-130° (dec.). Found: C 53.35; H 5.34; N 18.20%. $C_{20}H_{14}N_6O_6S \cdot 2C_3H_9N$. Calculated: C 53.42; H 5.48; N 19.20%.

Complex IV. This complex was obtained as a brown powder that rapidly lost NH_3. It decomposed in air in 30 min to give starting hydrazine I, which was identified from a mixed melting-point determination with an authentic sample.

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