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scheme: Hexaarylethanes (I), tetraarylhydrazines (II), and diarylnitrogen N-oxide (III), showing the effect of substituents X in phenyl rings on dissociation and stability. Electron-donor substituents in phenyl rings: $X = CH_3-$, CH_3O-, $(CH_3)_2N-$. Electron-acceptor substituents in phenyl rings: $X = -NO_2$, phenyl, etc. Donor substituents weaken dissociation for hexaarylethanes, intensify dissociation for tetraarylhydrazines, and diminish stability for the N-oxide; acceptor substituents intensify dissociation for hexaarylethanes, weaken dissociation for tetraarylhydrazines, and increase stability for the N-oxide.

Figure 1: scheme: Hexaarylethanes (I), tetraarylhydrazines (II), and diarylnitrogen N-oxide (III), showing the effect of substituents X in phenyl rings on dissociation and stability. Electron-donor substituents in phenyl rings: $X = CH_3-$, CH_3O-, $(CH_3)_2N-$. Electron-acceptor substituents in phenyl rings: $X = -NO_2$, phenyl, etc. Donor substituents weaken dissociation for hexaarylethanes, intensify dissociation for tetraarylhydrazines, and diminish stability for the N-oxide; acceptor substituents intensify dissociation for hexaarylethanes, weaken dissociation for tetraarylhydrazines, and increase stability for the N-oxide.

Abstract

Full Text

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ON THE STRUCTURE, PROPERTIES, AND ABILITY TO DISSOCIATE INTO FREE RADICALS OF CERTAIN HYDRAZINE DERIVATIVES

On the question of the relationship between chemical structure and the ability to form free nitrogen radicals

(Presented by Academician I. N. Nazarov on 20 XI 1956)

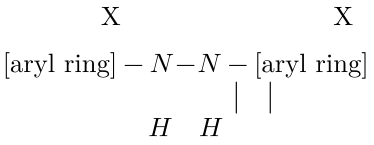
As was already mentioned in the preceding communication (^{1}), the free radicals of nitrogen include diarylnitrogens, formed upon dissociation of tetraarylhydrazines of general formula (II). Radicals of this group were discovered

in 1911 and studied in detail by Wieland and co-workers ($^{2-5}$); however, the question has remained unclear up to the present as to the causes of the fact known in the literature concerning the opposite character of the regularities in the dissociation into free radicals of molecules of hexaarylethanes (I), tetraarylhydrazines

(II) and diarylazote N-oxides (III), depending on the structure of the substituents in the phenyl rings (X). The following scheme clearly shows the existing interrelation between the nature of the substituent groups and the ability to form free radicals in this series of compounds.

In order to elucidate experimentally the causes with which the indicated facts are connected, we studied the chemical transformations, the capacity for polarographic reduction, and measured the dipole moments for a specially selected group of substances of the series of di- and tetrasubstituted hydrazines.

A central place among the substances investigated was occupied by the so-called "model" substances—tetraphenylhydrazine (II, X=H), moderately dissociating into two molecules of diphenylazote; tetra-*p*-nitrophenylhydrazine (II, $X=NO_2$), incapable of dissociation into radicals, and tetra-*p*-anisylhydrazine (II, $X=OCH_3$), possessing an increased capacity for dissociation into free radicals, as well as the corresponding substituted diphenylhydrazines of the general formula (IV).



$$\overset{X}{[\text{aryl ring}]} - \underset{H}{N} - \underset{H}{N} - \overset{X}{[\text{aryl ring}]}$$

IV

All substances were synthesized according to the procedures described in the literature (^{2}, ^{3}, ^{5}-^{10}), with the exception of tetraethylhydrazine, which was obtained by direct oxidation of diethylamine with potassium permanganate.

The principal methods of investigation chosen were polarographic reduction at a dropping mercury electrode, which makes it possible to characterize the strength of the N—N bond, and measurement of dipole moments, which makes it possible to elucidate the question of the spatial configurations of the compounds under consideration.

Table 1

Names of substances	Half-wave potential, corresponding to reduction of the N—N bond in hydrazines, in volts relative to n.c.e.; in acetate buffer pH = 4.25	Half-wave potential, corresponding to reduction of the N—N bond in hydrazines, in volts relative to n.c.e.; in ammonia buffer pH-8.04	μop · 10^{18}
Hydrazine	−1.34	−1.49	1.9
Phenylhydrazine	−0.15	–	–
Hydrazobenzene	−0.20	−0.25	1.85
Tetraphenylhydrazine	−0.61	−0.82	1.27
n, *n′*-Dinitrodiphenylhydrazine	−0.93	−0.97	–
Tetra-*p*-nitrophenylhydrazine	−1.22	−1.64	4.15
n, *n′*-Dimethoxyhydrazobenzene	−1.27	–	2.27
Tetra-*p*-anisylhydrazine	−0.62	−0.82	1.30
Diethylhydrazine	–	−0.16	0.51
Tetraethylhydrazine	–	−0.18	1.62
Diacetylhydrazine	−0.13	−0.18	–

The results of polarographic reduction of hydrazine derivatives, carried out on a Heyrovský micropolarograph in acetate and ammonia buffer solutions, are given in Table 1.

As a result of the polarographic reduction of hydrazine derivatives, the following principal observations were made.

1) Any substitution of the hydrogens of hydrazine (whether mono-, di-, or tetra-) leads to facilitation of reduction at the dropping mercury electrode.

2) In a series of diaryl-substituted hydrazines, upon introduction into the *p*-positions of the phenyl rings of an electron-accepting nitro group conjugated with the rings, the half-wave potential is shifted toward positive values, i.e., reduction of the N—N bond is facilitated. Upon introduction of an electron-donating methoxy group, the opposite picture is observed—a sharp shift of the potential toward negative values (Table 2).

3) In going from disubstituted hydrazines to tetrasubstituted ones, the influence of substituents on the strength of the N—N bond changes unexpectedly, namely: the presence of nitro groups in the *p*-position of the phenyl ring, instead of sharply facilitating the reduction reaction, leads to

a shift of the half-wave potential toward negative values and, conversely, introduction of methoxy groups into the same positions does not give the expected hindering of reduction of the N—N bond on a mercury dropping electrode (Table 2). On the basis of these data, it may be assumed that in tetraarylhydrazines, in contrast to diarylhydrazines, electron-accepting nitro groups and electron-donating methoxy groups, owing to some factors, are removed from conjugation with the p-electrons of the central nitrogen atoms and do not exert their usual electron-accepting or electron-donating action.

Table 2

Compounds	Half-wave potentials in volts relative to the n. c. e.	Half-wave potentials in volts relative to the n. c. e.	Half-wave potentials in volts relative to the n. c. e.
	$X = H$	$X = OCH_3$	$X = NO_2$
[structural formula: diarylhydrazine with substituent X in the phenyl rings and H at nitrogen]	−0.20	−1.27	−0.44
[structural formula: tetraarylhydrazine with substituent X in the phenyl rings]	−0.61	−0.62	−1.22

For the purpose of experimentally confirming this assumption for some of the compounds mentioned, dipole moments were measured. The measurements were carried out by the beat method in benzene at 25° (see Table 1).

Fig. 1. *a* and *b*—the N—N axis lies in the plane of the drawing; *c*—the N—N axis is perpendicular to the plane of the drawing.

Trans form *Cis form* *Average*
nitrogen atom hydrogen atom

Comparison of the experimental values of the dipole moments with those calculated by the vector-sum method for three different configurations of hydrazines, schematically shown in Fig. 1, and examination of spherical models of the molecules made it possible to discover interesting facts.

It turned out that almost all of the hydrazine derivatives considered, as well as the simplest hydrazine itself (11), do not have free rotation of the dipoles with respect to the N—N bond and, at the same time, do not have what would appear to be the most energetically favorable trans configuration (Fig. 1, *a*). Examination of models of tetraarylhydrazine molecules shows that the reason for this is steric hindrance, which occurs both in the case of the cis and in the case of the trans configuration.

Steric hindrance is especially clearly expressed in the case of tetra-*p*-nitrophenylhydrazine (II, X = NO_2). The dipole moments calculated for the cis and trans configurations are 6.72 D and 0, respectively, while the experimental dipole moment is 4.15 D.

It follows from this that the cis and trans arrangement of the molecule is impossible here (apparently, a considerable effect of repulsion of the nitro groups is manifested), and the only possible configuration of the molecule is the so-called "average" one (Fig. 1, *c*; μ__calc = 4.10 D). The presence of this config-

configuration, in turn, almost completely excludes the possibility of p-π conjugation (the axes of the p- and π-electron clouds are almost perpendicular). This also leads to the fact that the influence of nitro groups, as electron-acceptor substituents, on the $N = N$ bond is not manifested at all; the electron density remains the same as in unsubstituted hydrazine, and its reduction at the dropping mercury electrode occurs at a very negative potential ($E_{1/2}$ of hydrazine = −1.36 V; $E_{1/2}$ of tetra-*p*-nitrophenylhydrazine = −1.22 V), whereas in n, n'-dinitrodiphenylhydrazine the nitro groups considerably facilitate reduction.

On this basis it may be assumed that the inability of tetra-*p*-nitrophenylhydrazine to dissociate into free radicals is not at all due to the electron-acceptor nitro groups in tetra-*p*-nitrophenylhydrazine failing to exhibit an effect opposite to that in hexaaryl-substituted ethane, but is a consequence of spatial factors leading to the absence of p-π conjugation in the molecule.

In the case of tetra-*p*-anisylhydrazine (II, $X = OCH_3$) there is a configuration intermediate between the fully trans and the mean configuration ($\mu_{\text{expt}} = 1.30$ D, $\mu^{\text{av}}_{\text{calc}} = 0.85$ D). In terms of the conditions for conjugation it is analogous to the configuration of tetraphenylhydrazine. Because of steric factors, the methoxy groups are taken out of conjugation, owing to which the half-wave potentials of these compounds are nearly identical ($E_{1/2}$ of tetraphenylhydrazine = −0.61; $E_{1/2}$ of tetra-*p*-anisylhydrazine = −0.62), whereas in the corresponding disubstituted compound (IV, $X = OCH_3$) the methoxy groups distinctly exhibit their electron-donor effect and greatly hinder reduction at the dropping mercury electrode.

Thus, the results obtained by us show that, among the causes responsible for the opposite influence of identical substituents on the tendency toward dissociation into free radicals in the series of tetraaryl-substituted hydrazines (II), as compared with hexaaryl-substituted ethane (I), spatial factors are of substantial importance.

On the basis of a generalization of the experimental data obtained on the physicochemical properties of the substances under consideration and of literature information on the chemical features of radicals of the diphenyl nitrogen series, it may be suggested that the previously drawn conclusion regarding the opposite influence of the nature of substituents on the stability of free radicals of the triphenylmethyl and diphenyl nitrogen series is not justified, since the significance of spatial factors was not taken into account.

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