RUSSIAN
CHEMICAL
REVIEWS
Uspekhi Khimii

February 1972

U.D.C. 541.623 : 547.556.3

Tautomerism of Aromatic Azo-compounds

I.Ya.Bershtein and O.F.Ginzburg

Recent results on the tautomeric properties of aromatic azo-compounds in neutral and acid solutions are reviewed. The tautomerism of the conjugate acids of azo-compounds (the *trans*-azonium cations) is discussed, and also the tautomeric equilibria between azo-forms and quinone hydrazones in acid solutions of *p*-aminoazo-compounds and in neutral solutions of hydroxyazo- and aminoazo-compounds. Available qualitative and quantitative results on the effects of substituents and of the properties of the medium on the position of tautomeric equilibrium are compared. The problem of applying correlation analysis to tautomeric systems is analysed. A list of 179 references is included.

CONTENTS

I. Introduction	97
II. Tautomerism of hydroxyazo-compounds	98
III. Tautomerism of aminoazo-compounds	101
IV. Tautomerism of conjugate acids of azo-compounds	101
V. Tautomerism of conjugate acids of *p*-aminoazo-compounds	103

I. INTRODUCTION

Azo-compounds constitute an extraordinarily interesting and important class of compounds from both practical and theoretical points of view. The ready availability, cheapness, and versatility of properties have guaranteed to azo-compounds a high proportion of the range of organic dyes manufactured by industry[1]. Azo-compounds have found wide application in the laboratory as acid–base, redox, metallochrome, and other indicators, stains for bacteriological and histological investigations, standard materials in adsorption chromatography, etc.

The study of azo-compounds has been of great value for the development of theoretical organic chemistry. Together with triphenylmethane, keto–enolic, and certain other classes of compounds, azo-compounds have been widely used in developing and testing theories of colour and constitution, indicator action, and acid–base and tautomeric transformations.

The tautomeric properties of certain aromatic azo-compounds were detected as early as the beginning of the twentieth century. Hantzsch and several other investigators (see list of references[2]) studied the tautomerism of the conjugate acids of *p*-aminoazo-compounds. Somewhat later[3] tautomerism was confirmed between azoid and quinone hydrazone forms in neutral solutions of hydroxyazo-derivatives of naphthalene. Finally, the tautomerism of the conjugate acids of *trans*-azo-compounds was studied as early as the 1960s.[4]

It can be stated without exaggeration that almost all known methods of investigating tautomeric equilibrium have been used for the quantitative and qualitative study of tautomeric relations in various classes of azo-compounds. Many of these methods were in fact first developed in connection with azo-compounds.

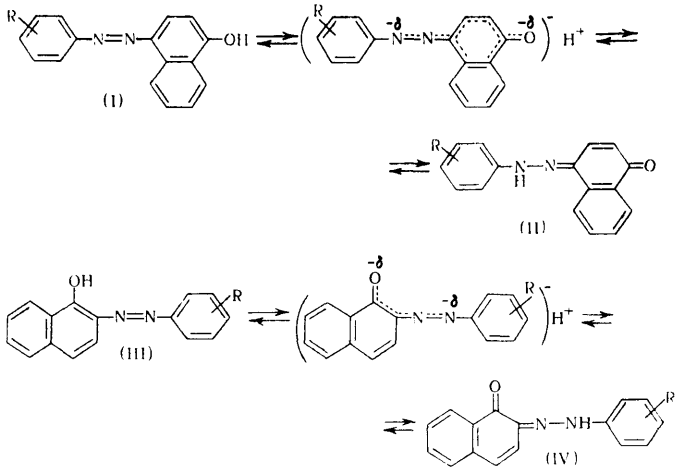
The total number of papers on the tautomerism of aromatic azo-compounds can hardly be fewer than those on classical keto–enol tautomerism. However, no

reviews are available on the present state of this problem. The present survey deals mainly with papers dating from 1955 (up to the beginning of 1970 inclusive). Bibliographies of earlier investigations will be found in the monographs by Venkataraman[1] and by Zollinger[5] and also in reviews[2,6].

II. TAUTOMERISM OF HYDROXYAZO-COMPOUNDS

1. Hydroxyazo-compounds of the Naphthalene Series

A wide circle of investigators became interested in the tautomerism of hydroxyazo-compounds after Zincke and Bindewald[7] had shown that the same product is obtained by coupling the benzenediazonium ion with 1-naphthol and by condensing phenylhydrazine with naphtha-1,4-quinone. The structure of this product, which could be represented by either formula (I) or (II) (both with R = H) became a matter of controversy (lists of references will be found in papers[8,9] and in monographs[1,5]).



Zincke had already suggested[7] that a mobile equilibrium between the two forms might be established in solution. A similar suggestion was made for the product of the condensation of phenylhydrazine with naphtha-1,2-quinone, which proved to be identical with 2-phenylazo-1-naphthol (III: R = H). The concept of tautomerism between azo-forms (I and III) and quinone hydrazone forms (II and IV) in solutions of *p*- and *o*-hydroxyazo-compounds of the naphthalene series has since been put forward several times, but it became generally accepted after the classic work of Kuhn and Bär[3].

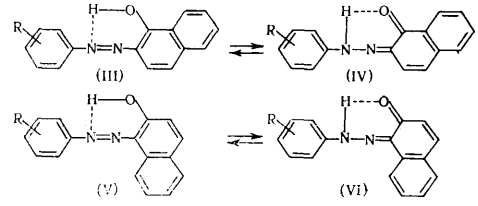
These workers suggested that the absorption spectrum of (I) should be analogous to that of its *O*-methyl ether, and the spectrum of (II) to that of its *N*-methyl derivative. On comparing the spectra of 4-phenylazo-1-naphthol in various solvents with the spectra of its *O*- and *N*-methyl derivatives, they concluded that the tautomeric equilibrium (I) $\rightleftharpoons$ (II) was established in all the solutions studied. The position of this equilibrium (according to modern views it should involve a common ion) depends in considerable measure on the nature of the solvent: e.g. it is displaced towards (I) in pyridine, but towards (II) in glacial acetic acid. In the case of *o*-hydroxyazo-compounds of the naphthalene series, according to these workers[3], the tautomeric equilibrium (III) $\rightleftharpoons$ (IV) is displaced in favour of the quinone hydrazone form (IV) in the majority of solvents.

The concept of tautomerism was developed in a large number of studies on the absorption spectra of *o*- and *p*-hydroxyazo-compounds of the naphthalene series[10-22]. The spectra of derivatives of 4-phenylazo-1-naphthol exhibit two maxima at 390–420 and 470–510 nm, due to the presence respectively of azoid and quinone hydrazone forms in solution. Variation in the polarity and also the solvating power of the solvent leads to a shift in the tautomeric equilibrium: the optical density at the absorption maximum of one form increases, while that at the maximum of the other form decreases. In some cases an isosbestic point is observed in the spectra with variation in the solvents (mixtures of alcohols with water[15,19]). Frequently, however, such a point cannot be distinguished, owing to the effect of the solvent on the spectra of the tautomers[3,14].

Increase in the polarity of the solvent displaces the equilibrium (I) $\rightleftharpoons$ (II) towards the more polar quinone hydrazone form. At the same time, the formation of hydrogen bonds with the solvent stabilises the azo-form. The overall sequence of solvents, producing an increasing proportion of the quinone hydrazone form according to Burawoy and Thompson[14], is—hexane < alcohol < benzene < chloroform < 50% aqueous alcohol < acetic acid. Increase in the alkalinity of the medium leads to a shift in the equilibrium towards the azo-form[21].

Solvation stabilisation of the quinone hydrazone form is prevented by substituents *ortho* to the azo-bond. Hence solvents have opposite effects on *o*- and *p*-hydroxyazo-compounds: in aprotic solvents the quinone hydrazone is preferred, but in alcohols the azo-form[14].

The influence of substituents on the equilibrium (I) $\rightleftharpoons$ (II) has been assessed from the relative intensities of the absorption maxima due to the two tautomeric forms[10,13,14,17,23]. Electron-donating *meta*- and *para*-substituents in the benzene ring of (I) increase the proportion of the azo-form; but electron-accepting substituents shift the equilibrium towards the quinone hydrazone form (II)

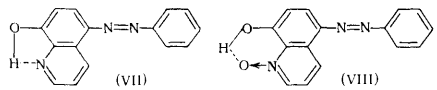


With *o*-hydroxyazo-compounds of the naphthalene series—notably with derivatives of 2-phenylazo-1-naphthol (III) and 1-phenylazo-2-naphthol (V)—the influence of solvents on the equilibria (III) $\rightleftharpoons$ (IV) and (V) $\rightleftharpoons$ (VI), and hence on the spectra of solutions of these compounds, is considerably smaller than in the case of *p*-hydroxyazo-compounds[3,13]. The explanation is that the tautomeric equilibrium of *o*-hydroxyazo-compounds is displaced to a considerable extent towards the quinone hydrazone forms[3,10,13,20].

The shift in equilibrium towards forms (IV) and (VI) of *o*-hydroxyazo-compounds is explained by the presence of a strong intramolecular hydrogen bond, first suggested by Oddo and Puxeddu[24]. This hypothesis has since been confirmed by a study of the infrared spectra[20,25-28]. An intramolecular hydrogen bond stabilises the quinone

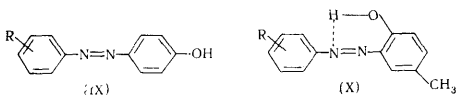
hydrazone form† and leads to a sharp decrease in the overall basic strength of the *o*-hydroxyazo-compound [30,31], together with the appearance of chelating properties. These are particularly strongly developed in *oo'*-dihydroxyazo-compounds, which are often used as analytical reagents for metals.

The intramolecular hydrogen bond in compounds of the type (III) and (V) forms part of a quasi-aromatic six-membered ring [32,33], the energy of formation of which may reach 16 kcal mole^{-1}. [33] This explains the absence of frequencies due to the hydroxy-group from the infrared spectra of *o*-hydroxyazo-compounds of the naphthalene series [27,34], the bathochromic shift in the ultraviolet spectra of *o*-hydroxyazo-compounds compared with the *para*-isomers [35], and also the difficulty of exchanging the hydroxyl hydrogen for deuterium by boiling in heavy water [36].



(VII) (VIII)

8-Hydroxy-5-phenylazoquinoline (VII) and especially its *N*-oxide (VIII) provide examples of intramolecular hydrogen bonds which stabilise azo-forms [16].



(IX) (X)

The influence of substituents on the strength of the hydrogen bond, and also the effect of the bond on the basic strength, have been assessed from the difference in basicity between the substituted *p*- and *o*-hydroxyazobenzenes (IX) and (X). [31,37] If the hydroxy-group has the same electronic effect in *para*- and *ortho*-positions, and the presence of an unchanged substituent—the 5-methyl group in (X)—can be neglected, the hydrogen bond in (X) can be characterised by the difference $pK_{(X)} - pK_{(IX)} = pK_H$.

Electron-acceptor substituents R produce a decrease in pK_H by diminishing the electron density on the nitrogen atom [31,37]. The correlation of pK_H with the σ-constants of the substituents is characterised by the parameter $\rho = -0.531$ [37] or -0.489 [31], while the relation $pK_{(X)} = f(\sigma)$ has $\rho = -1.21$ [37]. Comparison of these values confirms that the influence of substituents on the basicity of *o*-hydroxyazo-compounds is largely transmitted through the nitrogen atom and the hydrogen bond.

A similar conclusion was reached by Korolev and Stepanov [38], who used a two-parameter correlation of the pK_a of derivatives (X) with the σ^-- and σ-constants of the substituents. Here the σ^--constants represented the effects of substituents transmitted through the azo-group and the oxygen atom; while the σ-constants represented effects transmitted through one of the nitrogen atoms and the hydrogen bond. The values obtained for ρ_1 and ρ_2 were respectively -0.396 ± 0.108 and -0.757 ± 0.180.

Spectrophotometric data indicate [13] that the influence of the nature of substituents on the position of the (III) ⇌ (IV) equilibrium is similar to that found for the (I) ⇌ (II) equilibrium. Quantitative results have been obtained by means of ^{14}N-nuclear magnetic resonance spectroscopy (Table 1). Azobenzene and 10-*p*-methoxyphenylazo-9-phenanthrol were used as model compounds having an azoid and a quinone hydrazone structure. The presence of a mobile proton in the latter form impedes accurate determination of the signal to a greater extent the higher the concentration of this form. Therefore the values in Table 1 are insufficiently accurate for the application of correlation analysis to investigate the relation between the position of tautomeric equilibrium and the nature of the substituent.

Table 1. Content of quinone hydrazone form in solutions of 1-phenylazo-2-naphthol derivatives in deuterochloroform [39].

Substituent	Quinone hydrazone, %	Substituent	Quinone hydrazone, %
4'-CN	97	H	79
3'-CN	91	4'-Cl	78
3'-Cl	81	4'-Me	69
3'-Me	80	4'-OMe	52
3'-OMe	81	H (in hexane)	38

The proton magnetic resonance spectra could not be used for accurate determination of the position of tautomeric equilibrium [40,41], owing to rapid proton exchange between the two forms (lifetime of each form ~ 0.2 ms [39]).

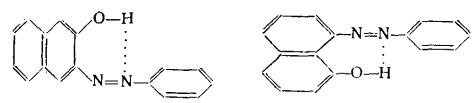
Studies have been made also of the polarographic behaviour [42,43], the surface tension of solutions [44], and the semiconductor characteristics of solid hydroxyazo-compounds [45,46]. These properties show little correlation with the tautomeric equilibrium position.

The ^{15}N-nuclear magnetic resonance spectra have been used to investigate the temperature dependence of the tautomeric equilibrium of 1-phenylazo-2-naphthol [47,48]. In dichloromethane the equilibrium shifts towards the quinone hydrazone form as the temperature falls ($\Delta H = 1.38$ kcal mole^{-1}). A similar conclusion was reached from a study of the absorption spectra at low temperatures [18,49]. With 4-phenylazo-1-naphthol cooling displaces the equilibrium towards the azo-form in ethanol, but towards the quinone hydrazone in methylcyclohexane ($\Delta H = 2 \pm 0.2$ kcal mole^{-1}) [18,50].

The basicity of derivatives of (V) has been studied in 50% aqueous ethanol [51], when the correlation

$$pK_a = 12.53 - 1.44\sigma^0 \quad (r = 0.99) \qquad (1)$$

was obtained. The dependence of the exponents of the effective basicity constants of a tautomeric mixture on the σ-constants of the substituents will be discussed in Section IV. Here we note merely that the linear relation (1) is due to a considerable shift in the equilibrium towards one of the tautomeric forms (cf. Table 1).



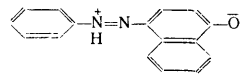
(XI) (XII)

3-Phenylazo-2-naphthol (XI) constitutes a special case among *o*-hydroxyazo-compounds of the naphthalene series.

† Quantum-chemical calculations by the Hückel molecular-orbital method, disregarding the effect of the hydrogen bond, predict for (III) that energy considerations will greatly favour the azo-form. With 4-phenylazo-1-naphthol the conjugation energy is similar for the two forms [29].

The diminished order of the 2–3 bond in naphthalene is responsible for the existence of (XI) only in the azo-form[52,53]. The presence of a hydrogen bond in (XI) has been proved by means of the infrared spectra[53] and is apparent in the lower activation energy of *cis–trans* isomerisation of (XI) in comparison with its *O*-methyl ether[54]. A similar phenomenon—the presence of a hydrogen bond in the absence of azo-quinone hydrazone tautomerism—has been shown also with *peri*-hydroxyazo-compounds of the naphthalene series (XII).[55]

Formulae (II), (IV), and (VI) probably do not represent accurately the structure of the quinone hydrazone forms of hydroxyazo-compounds. The lower frequency and intensity of vibrations of the CO group in the infrared spectra of (I) and (V)[26,53] indicate that zwitterionic structures of the type



(XIII)

which diminish considerably the order of the C=O bond, make a large contribution, a conclusion supported by measurements of the dipole moments of (I).[56] Since the hydroxy-group is a strong electron-donor substituent, there is no need to take into account the possible appearance of hydrazone tautomers with the proton on the α-nitrogen atom (Section IV).

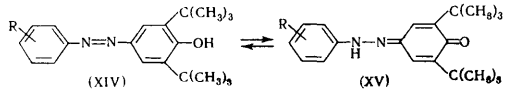
Infrared spectra indicate that hydroxyazo-compounds which are capable of tautomerism are present in the solid state as quinone hydrazones or as tautomeric mixtures[15].

2. Hydroxyazo-compounds of the Benzene and Anthracene Series

It has been concluded, from a comparative study of the ultraviolet spectra of hydroxyazobenzene, its derivatives, and their *O*-methyl ethers[10,11,22,57–59], proton magnetic resonance[40] and infrared[60] spectra, and polarographic investigation[42,43], together with a study of *cis–trans* isomerisation[61,62], that both *ortho*- and *para*-hydroxy-derivatives of azobenzene exist in the azo-form. The weak fluorescence observed with *o*- and *p*-hydroxyazobenzene[49] suggests that their solutions may contain very small quantities of the quinone hydrazone forms. True azo-compounds are incapable of fluorescence, which, on the other hand, is characteristic of all compounds having a hydrazone structure.

Dual reactivity is probably the explanation of published information on the reaction of 4-hydroxy-2′(or 4′)-nitroazobenzene derivatives with 2,4-dinitrophenylhydrazine[63] and also on their Diels–Alder reaction with cyclopentadiene[64].

The only known exception among hydroxyazo-compounds of the benzene series is provided by derivatives of 2,6-di-t-butyl-4-hydroxyazobenzene (XIV), for which the equilibrium

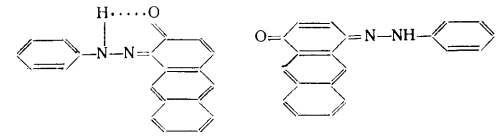


(XIV) (XV)

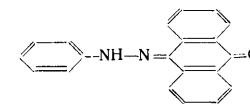
has been demonstrated (for all R other than $N(CH_3)_2$ and OCH_3)[65]. This exception is explained by the greater tendency of sterically hindered phenols to pass into quinoid forms[66]. The corresponding equilibrium constants, determined spectrophotometrically[67], show that the introduction of electron-acceptor substituents R increases the proportion of (XV), as with hydroxyazo-compounds of the naphthalene series.

Investigation of the basicity of *o*- and *p*-hydroxyazobenzene derivatives revealed in all cases a linear dependence of pK_a on the σ-constants of the substituents[31,37,68,69]. In 96–100% sulphuric acid doubly charged cations may be formed, probably by protonation not only of the azo-group but also of the hydroxyl[70].

When the absorption spectra of the products obtained by coupling 1-, 2-, and 9-anthrols with the benzenediazonium ion are compared with those of their *O*-acetyl derivatives, it is evident that *p*-hydroxyazo-compounds of the anthracene series exist predominantly in the quinone hydrazone form[11,71,72]. The tautomeric properties of (XVI) are confirmed by the strong fluorescence of its solutions, and also by the fact that the product (XVI) obtained by condensing phenylhydrazine with anthraquinone is identical with 10-phenylazo-9-anthrol prepared by azo-coupling[73].

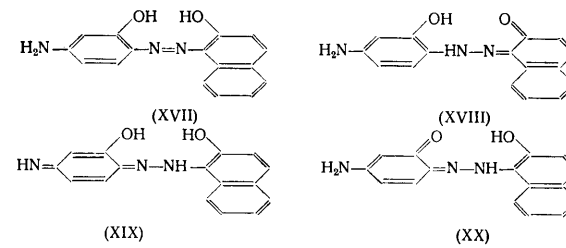


$\lambda_{max} = 511$ nm[11] $\lambda_{max} = 506$ nm[11]



(XVI)

The displacement of the tautomeric equilibrium towards the quinone hydrazone form on passing from hydroxyazo-derivatives of benzene to those of polyacenes was attributed by Ospensen[11] to a fall in the redox potential of the corresponding quinones on passing from *p*-benzoquinone (E_0 = 0.715 V, alcohol) to naphtha-1,4-quinone and anthra-1,4-quinone (0.484 and 0.401 V). This rule breaks down when we compare *p*- and *o*-hydroxyazo-derivatives of naphthalene with the redox potentials of the *o*-naphthaquinone (0.555 V, water) and *p*-naphthaquinone, which is explained by the presence of an intramolecular hydrogen bond in the *o*-hydroxyazo-compound. Similar results on a shift in the tautomeric equilibrium on passing from hydroxyazo-derivatives of benzene to those of naphthalene and anthracene were obtained[74] in a study of monolayers of azo-compounds having long alkyl groups.



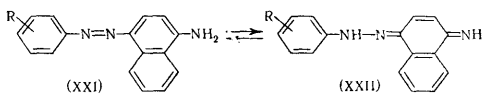
(XVII) (XVIII)

(XIX) (XX)

An interesting case of tautomerism has been described recently by Dedkov and Kotov[75] with 1-*p*-amino-*o*-hydroxyphenylazo-2-naphthol, for which the four tautomeric forms (XVII)–(XX) are possible. The ultraviolet spectra, supported by Hückel molecular-orbital calculations, indicate that three forms (XVII)–(XIX) are in equilibrium in the proportions 1 : 1.2 : 1.25.

III. TAUTOMERISM OF AMINOAZO-COMPOUNDS

The possibility of tautomerism between the azo-form (XXI) and the quinone hydrazone (XXII) in neutral solutions of *o*- and *p*-aminoazo-compounds of the naphthalene series has been investigated by many workers, mainly by comparing the absorption spectra of the compounds, their *N*-acetyl derivatives [35,71,76,77], and their *NN*-dimethyl derivatives [35] with those of the corresponding azo-compounds containing no auxochromic group [78,79]. Most authors have concluded that the quinone hydrazone form (XXII) is absent from solutions of *p*-aminoazo-derivatives of naphthalene.

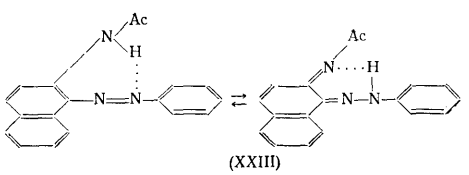


(XXI) (XXII)

No definite conclusion can yet be reached concerning *o*-aminoazo-compounds. There are results indicating that they exist in the quinone hydrazone form containing an intramolecular hydrogen bond [35], and also that tautomerism is absent in this case [78,80]. The presence of a strong intramolecular hydrogen bond in the naphthalene derivatives is confirmed by infrared spectroscopy [81,82].

The existence of aminoazo-compounds in the azo-form is confirmed by comparing their dipole moments with those of the corresponding aniline derivatives [83] and also by polarographic investigations [84]. Filippychev [85] reported that the solid hydrazone forms (XXII) could be obtained by heating the compounds in concentrated hydrochloric acid. The products could not be diazotised. However, no elementary analysis or other evidence of structure was given [85].

The *N*-acyl derivatives cannot be regarded as model compounds having an undoubted azo-structure. By diminishing the basic strength of the amino-group and thereby levelling out those of the two reaction centres [86] the acyl group makes azo–quinone hydrazone tautomerism more probable. Skulski and Urbanski [77] have mentioned the possibility of such tautomerism with 2-acetamido-1-phenylazonaphthalene

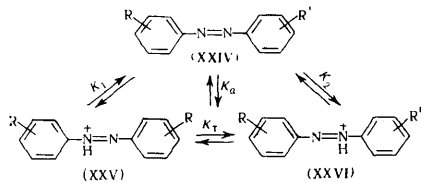


(XXIII)

Spectroscopic results indicate that aminoazo-derivatives of anthracene are probably capable of tautomerism with quinone hydrazone forms [71,72], but this equilibrium has not been examined in detail.

IV. TAUTOMERISM OF CONJUGATE ACIDS OF AZO-COMPOUNDS

Salt formation by azo-compounds in concentrated mineral acids has been known for a long time [87–89], but the structure of the products has only recently become a matter of controversy. If it is postulated that an azo-group contains two potentially basic centres, monosubstituted and unsymmetrically disubstituted azobenzenes (XXIV) may be expected to form two tautomeric conjugate acids (XXV) and (XXVI):



(XXIV) (XXV) (XXVI)

The effective basicity constant K_a and the tautomeric equilibrium constant K_T will then be related to K_1 and K_2 by the formulae [90]

$$K_a = \frac{K_1 \cdot K_2}{K_1 + K_2} \tag{2}$$

$$K_T = \frac{[XXV]}{[XXVI]} = \frac{K_2}{K_1} \tag{3}$$

Jaffé and his coworkers used correlation analysis to examine the possibility of the tautomerism (XXV) ⇌ (XXVI) in the cases of monosubstituted [91] and disubstituted [68] azobenzenes. If the influence of the substituents on the acid–base properties of these tautomers is described by Hammett's equation

$$pK_1 = (pK_1)_0 - \rho_1\sigma \tag{4}$$

$$pK_2 = (pK_2)_0 - \rho_2\sigma \tag{5}$$

and (4) and (5) are expressed as powers of 10, on substituting for K_1 and K_2 in Eqn. (2), we obtain

$$K_a = \frac{(K_1)_0 (K_2)_0 \cdot 10^{(\rho_1+\rho_2)\sigma}}{(K_1)_0 10^{\rho_1\sigma} + (K_2)_0 10^{\rho_2\sigma}} \tag{6}$$

or, taking logarithms,

$$pK_a = (pK_1)_0 + (pK_2)_0 - (\rho_1 + \rho_2)\sigma + \lg[(K_1)_0 10^{\rho_1\sigma} + (K_2)_0 10^{\rho_2\sigma}] \tag{7}$$

Equation (7) shows that the dependence of the exponents of the effective basicity constants of the tautomeric system on the σ-constants of the substituents is represented by a curve having the straight lines (4) and (5) as asymptotes. Analysis of Eqn. (7) by Kabachnik [92,93] and by Jaffé [91,94] indicates that this generally non-linear relation becomes linear when

$$\rho_1 = \rho_2 \tag{8}$$

i.e. when the substituents do not affect the position of the tautomeric equilibrium. Furthermore, the curvature of the pK_a–σ relation becomes slight with closely similar values of ρ_1 and ρ_2, with a considerable shift in the equilibrium towards one of the tautomers

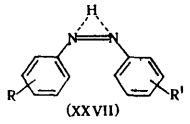
$$K_1 \gg K_2 \quad \text{or} \quad K_1 \ll K_2 \tag{9}$$

and finally with large absolute values of ρ_1 and ρ_2. [95] In all these cases the dependence of pK_a on σ for the tautomeric systems can be represented approximately by a straight line with a high correlation coefficient‡.

Jaffé and his coworkers [68,91] showed that values of pK_a for salt formation by a large number of azobenzene derivatives vary linearly with the σ^+-constants of the substituents (in the case of disubstituted derivatives the sum of

‡ By plotting model curves of Eqn. (7) we have shown that, if the experimental error is taken into account, the curvature becomes significant when very narrow boundary conditions, $|\rho_1 - \rho_2| \geq 2$ and ρ_1 or $\rho_2 < 3$, are satisfied simultaneously. For the compounds studied K_T varies between 0.3 and 3.

the σ^+-constants was taken) (Fig. 1). Since in this case it could not be predicted *a priori* that condition (8) or (9) would be satisfied, these workers concluded that the azo-group acts as a single reactive centre in salt formation. The structure of the conjugate acids of azobenzene and its derivatives would then be represented by the formula



(XXVII)

in which the proton is attached to both nitrogen atoms.

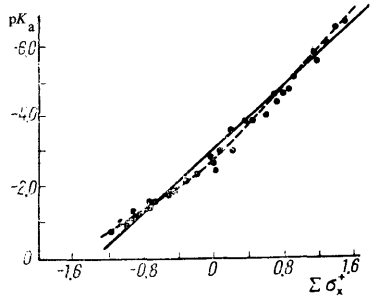
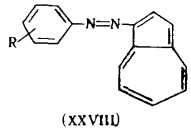


Figure 1. Dependence of pK_a for substituted azobenzenes on the σ^+-constants of the substituents[68] (sulphuric acid containing 20 vol.% of alcohol). The broken curve has been plotted from Eqn. (7) with $\rho_1 = 1.7$ and $\rho_2 = 3.0$ (see Section IV).

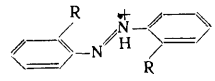
A linear dependence of pK_a on σ was found also by Gerson and Heilbronner[96] when studying the basicity of substituted phenylazoazulenes



(XXVIII)

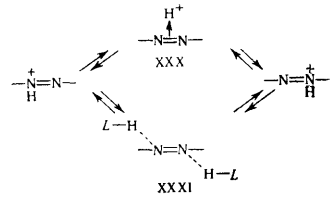
The azobenzene cation has subsequently been assumed to have a symmetrical structure in order to explain differences in the spectra of the conjugate acids of azobenzene and benzylideneaniline[97], and also in quantum-mechanical calculations of the spectra of azobenzene in concentrated sulphuric acid[98]. Simultaneous attachment of the proton to the lone pairs of both nitrogen atoms requires that the conjugate acid of azobenzene should have the *cis*-configuration, independently of the configuration of the original base. In 1960, however, Lewis[99] and Gerson et al.[100] showed simultaneously that *trans*- and *cis*-azobenzene form two conjugate acids differing in absorption spectra and in basic strength. Thus formula (XXVII) was proved to be incorrect, at least for conjugate acids of *trans*-azo-compounds.

A detailed investigation of the structure of *trans*-azonium cations has been made by Haselbach and Heilbronner[4,101], several aspects of the problem being examined. With unsymmetrical *N*-protonation the equivalence of the two identical substituents in the *ortho*- and *ortho'*-positions with respect to the azo-group in the compound



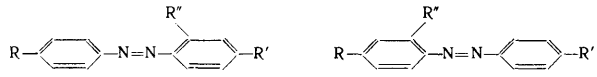
(XXIX)

should break down. Splitting of the signals due to protons in R should then be observed in the proton magnetic resonance spectra of (XXIX). Such splitting has been found with 2,2'-di- and 2,2',4,4'-tetra-methoxyazobenzenes in a mixture of trifluoroacetic and perchloric acids[4] and also with 2,2'-azoisobutane in 95% sulphuric and dideutero-sulphuric acids[101]. The absence of splitting with a large number of other methylated azobenzenes was explained[4] by rapid proton exchange between the tautomeric forms. The intermediate state is the π-complex (XXX) (intramolecular rearrangement) or a complex with two solvated protons of the solvent (XXXI) (intermolecular rearrangement)[101]:



XXX XXXI

As other evidence of unsymmetrical protonation of the azo-group Haselbach[4] examines the change in basicity on the introduction of substituents at position 2 or 2' in an unsymmetrically substituted azobenzene. If protonation of the azo-group is symmetrical, the compounds



(XXXII) (XXXIII)

should be similar in basicity. In fact (XXXII) and (XXXIII) differ in basic strength, to a greater extent the greater the difference between the properties of the substituents R and R'. With $\sigma_R - \sigma_{R'} = 1.56$, for example, the difference $pK_{(XXXII)} - pK_{(XXXIII)} = 1.90$.[4]

Finally, accepting the hypothetical unsymmetrical protonation of the azo-group, Haselbach attempted to estimate separately the effects of substituents on the nearer and on the more remote nitrogen atom by means of the arbitrary parameters R_α and R_β. He treated basicity data on 57 azobenzene derivatives by the method of least squares, and after several successive approximations he obtained values of R_α and R_β for the 4-substituents—methyl (−0.21 and −0.75), methoxyl (−0.31 and −1.85), and nitro (1.37 and 2.76).[4] This worker regards the statistically significant difference in the quantities R_α and R_β as confirmation of the starting hypothesis of unsymmetrical *N*-protonation.

On the assumption of a parallelism between the effects of substituents in the benzylideneaniline and azobenzene series Haselbach used data on the basic strengths of the former derivatives[101-103] to obtain the Hammett parameters $\rho_\alpha = 1.74$ and $\rho_\beta = 2.99$ for the effects of substituents on the basicities of the nearer and more remote nitrogen atom of the azo-group[4].

Since benzylideneaniline derivatives have a non-planar structure, in contrast to azo-compounds, the values obtained by Haselbach are extremely rough approximations. However, the following important conclusions can be reached on their basis. Thus if Eqn. (7) is plotted with $\rho_1 = 1.7$ and $\rho_2 = 3.0$ (broken curve in Fig. 1), it can be

concluded that Jaffé's results can be represented by this equation, and hence are consistent with the tautomerism (XXV) ⇌ (XXVI).

Since azobenzene itself is symmetrical, $(K_1)_0 = (K_2)_0$ in Eqns. (4) and (5). Substituting the values of ρ_α and ρ_β in these equations, we find that, when a substituent having $|\sigma| = 0.5$ is present in the azobenzene molecule, the content of one of the tautomeric forms is less than 20% ($K_T > 4.4$ or < 0.2). When the σ-constant of the substituent (or the difference between those of two substituents in different benzene rings) is unity, the position of tautomeric equilibrium will shift to 95% or more of one of the tautomers.

Unsymmetrical protonation of the azo-group is consistent with the proton magnetic resonance spectra of *p*-hydroxyazobenzene derivatives[104], the basic strengths and rates of oxidation of a series of azobenzene derivatives[105], and also the infrared spectra and the structure of complexes of azo-compounds with metal halides[106].

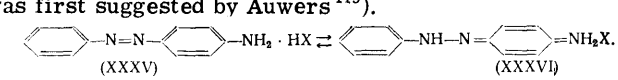
Thus it can be accepted as established that the protonation of *trans*-azo-compounds in concentrated acids is accompanied by the formation of a tautomeric mixture of the two cations (XXV) and (XXVI). This conclusion cannot be extended to the conjugate acids of *cis*-azo-compounds. Collins and Jaffé[107] showed that the basic strengths of *trans*-azo-compounds are correlated by the σ^+-constants, and those of the *cis*-isomers by the σ^--constants. The explanation of this difference is that the azo-group is an electron-acceptor reactive centre in *trans*-azo-compounds, but in *cis*-azo-compounds with their non-planar structure[108] the possibility of competing n,π-conjugation of the lone electron pairs of the nitrogen with the benzene rings confers an electron-donor character on the azo-group.

The extraordinarily deep colour of *pp'*-bisdimethylaminoazobenzene (XXXIV) in acid solution ($\lambda_{max} = 670$ nm) led Cilento[109] to attribute a π-complex structure to the conjugate acid of this aminoazo-compound. However, other results[110,111] indicate that the properties of (XXXIV) are entirely consistent with those of other azo-compounds. Thus there is no need to assume a special structure for the conjugate acid in the case of (XXXIV).

An interesting but hitherto uninvestigated fact is the change in the spectra of azobenzene (and its derivatives) in oleum[89], which is attributed to the formation of a doubly charged salt.

V. TAUTOMERISM OF CONJUGATE ACIDS OF *p*-AMINOAZO-COMPOUNDS

Derivatives of *p*-aminoazobenzene have been widely used as indicators for almost a century[112]. After Thiele[113] had shown, and Hantzsch and Hilscher[87] had confirmed, that two series of isomeric salts§—yellow and reddish violet—can be isolated in the solid form from acid solutions of *p*-aminoazo-compounds, the hypothesis was put forward that the acid solutions contain two tautomeric forms, in which the proton is attached to the amino-group (XXXV) or to the azo-group (XXXVI) (the latter formula was first suggested by Auwers[115]).

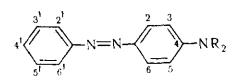


(XXXV) (XXXVI)

§ However, there is as yet no evidence that these salts differ in chemical structure. Their infrared spectra[114] suggest rather that the two series of salts of *p*-aminoazo-compounds are merely crystalline modifications.

This hypothesis is supported by spectroscopic investigations. The spectra of *p*-aminoazo-compounds in dilute acids exhibit two absorption maxima—in the region of 320 and 520 nm—in the range 300–600 nm[2] (Table 2). By analogy with azobenzene and its *p*-trimethylammonium derivative, whose spectra in neutral and weakly acid solutions have a maximum at 320 nm, the corresponding maximum in the spectra of *p*-aminoazo-compounds was assigned to the ammonium tautomer (XXXV). On the basis of a comparison with the spectra of azoanisole ($\lambda_{max} = 500$ nm[116]) and *p*-methylthioazobenzene (532 nm[117]) in concentrated acids, the maximum in the region of 520 nm was ascribed to the quinone hydrazone tautomer.

Table 2. Absorption spectra of some *p*-aminoazo-compounds in 50% alcoholic hydrochloric acid.



No.	4-Dimethylaminoazobenzene derivative	*C* line λ_{max} ($10^{-3}\varepsilon_C$)	*A* line λ_{max} ($10^{-3}\varepsilon_A$)	$\varepsilon_C/\varepsilon_A$	Ref.
1	(Aminoazobenzene)	500 (12.2)	320 (16.8)	0.73	131
2	(Dimethylaminoazobenzene)	20 (34.0)	320 (10.1)	3.4	131
3	(4-Ethylmethylaminoazobenzene)	516 (21.5)	318 (15.2)	1.4	131
4	(Diethylaminoazobenzene)	518 (9.50)	318 (19.5)	0.49	131
5	3-Methyl	508 (2.6)	a	—	148
6	3-Ethyl	490 (1.0)	a	—	148
7	3-Isopropyl	460 (0.6)	a	—	148
8	2-Methyl	512 (47.6)	330 (3.0)	15.9	118
9	2,6-Dimethyl	496 (53.2)	328 (2.0)	26.8	118
10	2'-Methyl	515 (5.10)	325 (17.6)	0.29	131
11	2'-Ethyl	510 (2.60)	332 (18.1)	0.14	131
12	2'-Carboxylic acid	518 (43.4)	325 (3.3)	13.1	131
13	3'-Ethoxy	522 (36.6)	318 (8.2)	4.5	131
14	3'-Nitro	500 (37.8)	312 (10.5)	3.6	131
15	4'-Methoxy	548 (18.5)	352 (18.2)	1.0	131
16	4'-Nitro	512 (61.6)	332 (7.10)	8.7	131

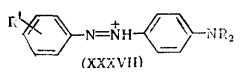
[a] Values not given in Ref. 148.

The absorption spectra of acid solutions of *p*-aminoazo-compounds were analysed in papers by Hantzsch (bibliography in Ref. 2), and the results have since been confirmed by many workers on a large number of compounds (see review[6]). This work demonstrated that the two maxima relate to different compounds. Thus Hantzsch noted long ago that increase in the acid concentration was accompanied by an increase in optical density at the 520-nm maximum but a decrease at the 320-nm maximum[2]. He interpreted this as due to a shift in the equilibrium in favour of the tautomer (XXXVI). A study of a series of methylated[118] and sulphonated[119] derivatives of *p*-dimethylaminoazobenzene showed that, if the introduction of a substituent into the molecule increases the molar extinction coefficient at 520 nm, the coefficient at 320 nm decreases. Conversely, if substitution produces a decrease in the coefficient at 520 nm, the extinction coefficient at 320 nm increases. This agrees well with the view that the solution contains two compounds, whose concentrations are interrelated.

It is now generally accepted that tautomerism occurs in acid solutions of *p*-aminoazo-compounds. Isolated papers in which salt formation by these compounds was regarded as involving addition of a proton solely to the amino-group[120–123] or solely to the azo-group[89,124,125] were

based on incomplete data or erroneous concepts. They have all been subjected to soundly based criticism[6,117,126,127].

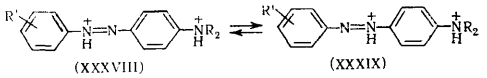
The possibility that the equilibrium may involve a tautomer with a proton attached to the α-nitrogen of the azo-group



(XXXVII)

can be assessed on the basis of the above analysis of the tautomerism of azonium cations (Section IV). Since the amino-group is a strongly electron-donating substituent (values of σ^+ for NH_2, $N(CH_3)_2$, and $N(C_2H_5)_2$ are respectively −1.3, −1.7, and −1.42[128]), it may be supposed that the proportion of the cation (XXXVII) in the tautomeric equilibrium of the conjugate acids of *p*-aminoazo-compounds should in most cases be insignificant. This conclusion is confirmed by quantum-mechanical calculations by the Hückel molecular-orbital method, which have shown that cation (XXXVII) is considerably less favoured energetically than are cations of the types (XXXV) and (XXXVI)[129].

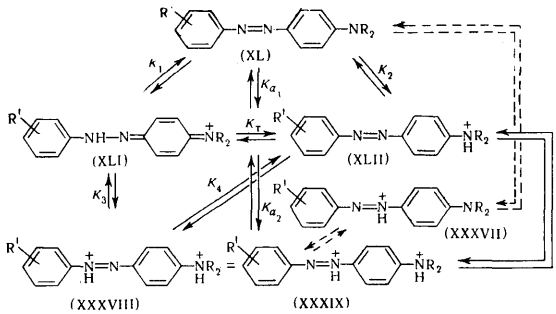
In concentrated mineral acids *p*-aminoazo-compounds add a second proton to form a doubly charged cation, whose structure is usually represented by the formula (XXXVIII). In view of the above discussion on the tautomerism of azonium cations, however, it must be assumed that a tautomeric equilibrium between the doubly charged cations (XXXVIII) and (XXXIX) is established in concentrated acids:



(XXXVIII) (XXXIX)

Whereas conversion of a *p*-aminoazo-compound into a monocationic salt will lead to a deepening of the colour of the solution from yellow to red-violet, addition of a second proton will [also] heighten its colour. The absorption maximum of the doubly charged cation usually lies in the range 410–440 nm,[130] which is approximately where the conjugate acid of azobenzene absorbs (435 nm).

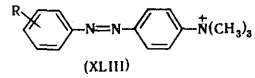
Thus the acid–base and tautomeric transformations of *p*-aminoazo-compounds (XL) can be represented over a wide range of acidities by the scheme



(XXXVIII) (XXXIX)

Values of pK_{a_1} for *p*-aminoazo-compounds vary in the range 1.8–2.5 (in 50% alcohol)[116,120,125,126,131,132]; those of pK_{a_2} lie either between −2.1 and −6.7 (aqueous sulphuric acid)[116,120,125] or between −2.3 and −8.5 (sulphuric acid containing 20 vol.% of alcohol)[95,133]. The acid–base properties of derivatives of *p*-aminoazobenzene have also been studied in aprotic solvents[134,135].

After completion of the first salt formation, changes occur in the solvation sheath of molecules of *p*-aminoazo-compounds in the acidity range $0 \geqslant H_0 \geqslant -1$. These changes are evident in the intensities of the absorption bands in the spectra of these compounds and also of *p*-phenylazophenyltrimethylammonium derivatives



(XLIII)

which are analogues of the ammonium tautomers (XLII)[130,133].

Pal'm and Khaldna[136,137] have studied similar changes with many organic bases in the same acidity range. The processes consist essentially in hydrogen bonding between the *p*-aminoazo-molecules and hydrated protons of the medium, which may be regarded as the initial stage of the second protonation.

Further increase in the acid concentration of the solution is accompanied by a shift in the equilibrium in favour of the tautomer (XLI)[68,126,131,138,139], which continues as far as the second salt formation (Fig. 2).

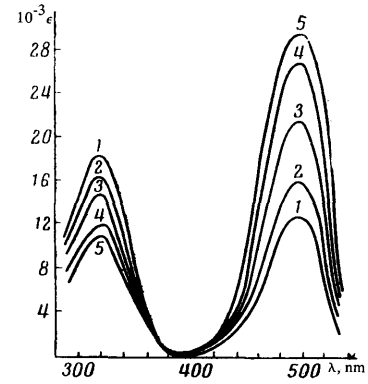


Figure 2. Absorption spectra of *p*-aminoazobenzene in different concentrations (*N*) of sulphuric acid: *1*) 3.2; *2*) 4.9; *3*) 6.5; *4*) 9.8; *5*) 10.7[160].

Most papers on tautomerism in acid solutions of *p*-aminoazo-compounds published during the past fifteen years had the aim of assessing quantitatively the position of the (XLI) ⇌ (XLII) equilibrium and the influence of substituents on this equilibrium. Since salt formation by *p*-aminoazo-compounds takes place almost instantaneously even at low temperatures[140], attention has been concentrated on physicochemical methods, mainly spectrophotometry. A substantial obstacle was the impossibility of obtaining a solution containing only one of the tautomers¶. It was therefore impossible to determine the molar extinction coefficients of the tautomers and to apply the usual methods of quantitative spectrophotometric analysis to the equilibrium.

¶ As Milliaresi and Izmail'skii assume[141], only the cation (XLI) is present in dichloromethane to which trifluoroacetic acid has been added, but its spectrum undoubtedly differs from the spectrum in aqueous solutions.

One attempt to avoid this difficulty was the method, used by several authors [142-146] and most consistently by Sawicki [117,127,131,147], of characterising the position of the tautomeric equilibrium by the intensity ratio of the absorption maxima corresponding to the two tautomers. The ratio ϵ_C/ϵ_A was employed, where ϵ_C and ϵ_A are the molar extinction coefficients of the solution at the absorption maxima of the quinone hydrazone and the ammonium tautomers respectively. It is easy to show that, if neither tautomer absorbs at the wavelength of maximum absorption by the other,

$$\frac{\varepsilon_C}{\varepsilon_A} = \frac{[XLI]}{[XLII]} \cdot \frac{\varepsilon_{XLI}}{\varepsilon_{XLII}} = K_T \frac{\varepsilon_{XLI}}{\varepsilon_{XLII}} \qquad (10)$$

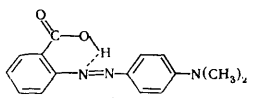
where $\epsilon_{(XLI)}$ and $\epsilon_{(XLII)}$ are the molar extinction coefficients of the tautomers at their maxima. The use of ϵ_C/ϵ_A instead of K_T is based on the postulate that the ratio $\epsilon_{(XLI)}/\epsilon_{(XLII)}$ is either constant or almost constant for all the compounds investigated.

Although such a postulate is admittedly inaccurate, it has helped to reveal several qualitative features of the effect of substituents in different positions in the molecule on the (XLI) ⇌ (XLII) equilibrium. Table 2 shows that replacing the hydrogen atoms of the amino-group by methyl groups creates a decrease in the proportion of the ammonium tautomer, probably owing to a diminution in its stabilisation by solvation energy [118]. Substitution of ethyl for methyl groups lowers ϵ_C/ϵ_A as a consequence of the larger positive inductive effect of ethyl groups, and perhaps partial emergence of the diethylamino-group from the plane of the molecule.

Substituents at position 3 or 5 in dimethylaminoazobenzene deflect the dimethylamino-group out of the plane of the benzene ring, thereby destroying its conjugation with the general π-system. Therefore the proportion of the quinone hydrazone tautomer falls with increase in the bulk of the substituent (compounds 5–7 in Table 2). This effect is present, although somewhat weaker, in aminoazobenzene derivatives [145]†.

Methyl groups at positions 2 and 6 greatly increase azo-protonation, which is explained by an increase in electron density on the β-nitrogen atom of the azo-group due to the $+I$-effect and hyperconjugation of the methyl groups [131]. In contrast, 2′-substitution sharply diminishes the proportion of the quinone hydrazone tautomer (compounds 10 and 11 in Table 2), which is interpreted by all authors as due to steric hindrance to attack by protons on the β-nitrogen atom, and also as indirect evidence of addition of the proton to the β- and not to the α-nitrogen atom. Furthermore, 2′-methyl groups somewhat disrupt the coplanarity of the molecule [104].

An exception among 2′-substituted derivatives is Methyl Red (No. 12 in Table 2). The sharp increase in ϵ_C/ϵ_A in this case is explained by the presence of an intramolecular hydrogen bond [142]



(XLIV)

Kipriyanov and Zhmurova [148] noted that even the 3-alkylation of (XLIV) does not appreciably diminish the proportion of the quinone hydrazone tautomer.

† It is interesting that 4-dimethylamino-3,5-dimethylazobenzene, which adds a proton only at the amino-group, does not possess the carcinogenic properties characteristic of most p-aminoazo-compounds [145].

The variation in ϵ_C/ϵ_A could not be used to indicate the effect of 3′-substituents, since the range of observable changes was narrow (compounds 13 and 14 in Table 2). Although this range is quite wide with 4′-substituted compounds, the conclusions reached by different workers [118,119,131,143] on the nature of the effect of 4′-substituents are often contradictory. The probable reason is that the constancy of the ratio $\epsilon_{(XLI)}/\epsilon_{(XLII)}$ originally postulated does not hold for these compounds. The most reliable conclusion is that the equilibrium (XLI) ⇌ (XLII) is displaced by electron-donor substituents in favour of the ammonium tautomer, and by electron-acceptor substituents towards the quinone hydrazone tautomer (compounds 15 and 16 in Table 2).

In a series of papers Jaffé and his coworkers [126,133,149-152] suggested two methods of using model compounds to determine K_T for the equilibrium (XLI) ⇌ (XLII). The compounds chosen as models were p-trimethylammonioazobenzene derivatives (XLIII), which are closely analogous to the ammonium tautomers (XLII). In the first of these methods, since used by Reeves [153], the molar extinction coefficients of the cations (XLII) and (XLIII) were equated:

$$\varepsilon_{(XLII)} = \varepsilon_{(XLIII)} \qquad (11)$$

The concentration of the ammonium tautomer was then calculated from the optical density of the solution of the p-aminoazo-compound at the wavelength of maximum absorption by the cation (XLII) (the total concentration of the tautomers was taken to be equal to the initial concentration of the base). This involved the assumption that the tautomer (XLI) did not absorb at this wavelength. Results [133] obtained by this method for a series of derivatives of dimethylaminoazobenzene in aqueous sulphuric acid containing 20 vol.% of alcohol are listed in column A of Table 3. An attempt was also made to allow for possible absorption by the tautomer (XLI) at the wavelength of maximum absorption by the tautomer (XLII). This absorption was assumed to be 2000 mole^{-1} cm^{-1} (from data for 4-amino-3,5-di-t-butylazobenzene, which was considered [126] to add a proton only at the azo-group). These results are listed in column B.

Table 3. Values of K_T for dimethylaminoazobenzene derivatives (aqueous sulphuric acid containing 20 vol.% of alcohol) [133].

Substituent (4′-)	A	B	C
CH_3O	0.53	0.60	2.39
CH_3	1.44	1.88	4.13
H	2.10	3.10	7.15
Cl	1.80	2.40	5.02
Br	2.61	3.86	6.05
CF_3	3.57	5.62	16.8
NO_2	4.36	7.00	57.9

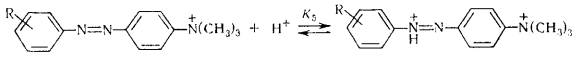
The second method proposed by Jaffé et al. utilised the pK_{a_2} values. Examining the formation of a dicationic salt of the p-aminoazo-compound (disregarding the presence of the tautomer XXXIX), Jaffé showed that

$$K_T = \frac{K_{a_2}}{K_4} - 1 \qquad (12)$$

(for notation see above scheme). Since K_4 was unknown, he assumed that

$$K_4 = K_5 \qquad (13)$$

where K_5 is the experimental equilibrium constant for



Values obtained for K_T by this method are given in column C of Table 3. They exceeded the spectrophotometric values by factors of 3–4. On comparing the results obtained, these workers were inclined to prefer the constants in column C.

A further defect of this work, in addition to the admitted inaccuracy of Jaffé's assumptions (Eqns. 11 and 13), is his neglect of the dependence of the position of tautomeric equilibrium on the concentration of acid in the solution. Nevertheless, the actual fact that the tautomeric equilibrium shifts with change in the acid concentration has enabled a method to be developed for determining K_T without the use of model compounds[154–156]. If the total concentration of tautomers in the solutions whose absorption spectra are illustrated in Fig. 2 is constant,

$$C_{XLI} + C_{XLII} = C_0 \qquad (14)$$

where C_0 is the initial concentration of the base, and Beer's law holds for both tautomers, the optical densities of these solutions are connected by a linear relation[67]. With the absorption maxima of the tautomers as analytical wavelengths (λ_{XLI} and λ_{XLII}), and provided that neither tautomer absorbs at the wavelength of maximum absorption by the other, the equation expressing this relation will be

$$\frac{D^{\lambda_{XLI}}}{\varepsilon^{\lambda_{XLI}}_{XLI}} + \frac{D^{\lambda_{XLII}}}{\varepsilon^{\lambda_{XLII}}_{XLII}} = C_0 d \qquad (15)$$

where the D are the optical densities of these solutions at λ_{XLI} and λ_{XLII}, the ϵ are the molar extinction coefficients of the tautomers (XLI) and (XLII) at these wavelengths, and d is the thickness of the cuvette. The validity of the assumption that one tautomer does not absorb at the wavelength of maximum absorption by the other can be checked by the method suggested in Ref. 67. Equation (15) enables us to find (either analytically or graphically) the quantities

$$D^{\lambda_{XLI}}_{max} = \varepsilon^{\lambda_{XLII}}_{XLI} C_0 d \qquad (16)$$

$$D^{\lambda_{XLII}}_{max} = \varepsilon^{\lambda_{XLII}}_{XLII} C_0 d \qquad (17)$$

which give the optical density of the solution at ϵ_{XLI} and ϵ_{XLII} if the equilibrium is completely displaced towards tautomer (XLI) (i.e. when $C_{XLI} = C_0$) or tautomer (XLII) (when $C_{XLII} = C_0$). After (16) and (17) have been evaluated, determining the molar extinction coefficients of the tautomers and calculating K_T in all the solutions investigated present no difficulty.

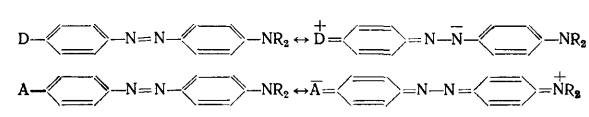
This method has been used to study the tautomeric equilibrium of several 3′- and 4′-substituted derivatives of aminoazobenzene, dimethylaminoazobenzene, and diethylaminoazobenzene[95,156,157]. Table 4 shows that 3′-substituents have little effect on the position of tautomeric equilibrium. In conformity with the discussion in Section IV, therefore, the dependence of pK_{a_1} on σ is linear for 3′-substituted dimethylaminoazobenzene[156]. The small changes in K_T with variation in the 3′-substitution from the nitro- to the methoxy-group suggests that the equilibrium (XLI) ⇌ (XLII) is insensitive to the inductive effect of the substituent.

This conclusion is supported by the correlations of $\lg K_T$ with the difference $\sigma^+ - \sigma_I$ or $\sigma^- - \sigma_I$ for +C and –C substituents respectively, which are found with 4′-substituted derivatives of dimethylaminoazobenzene and diethylaminoazobenzene[95,156] (Fig. 3). The dominant role of conjugation in the effect of substituents on the position of the tautomeric equilibrium of conjugate acids of *p*-aminoazo-compounds is consistent with the correlation found by Isaacs and Jaffé[133] between $\lg K_T$ and the σ^+- or σ^--constants ($r = 0.968$) for the approximate values of K_T determined by them for 4′-substituted dimethylaminoazobenzenes (Table 3, column C).

Table 4. Values of K_T with $H_0 = -1.20$ and parameters of Eqn. (18) for certain *p*-aminoazo-compounds[95] (values of H_0 from Ref. 159).

Substituent	*a*	*b*	*r*	K_T
p-Aminoazobenzene derivatives				
H	—0.620	0.217	0.995	0.44
3′-NO_2	—0.673	0.209	0.995	0.38
p-Dimethylaminoazobenzene derivatives				
H	0.241	0.104	0.994	2.3
4′-CH_3	0.078	0.102	0.993	1.6
4′-OCH_3	—0.066	0.091	0.974	1.1
4′-Br	0.127	0.114	0.998	1.8
4′-F	—0.305	0.090	0.976	0.65
4′-SO_3Na	0.457	0.080	0.983	3.7
3′-OCH_3	0.195	0.100	0.997	2.1
3′-Cl	0.273	0.114	0.976	2.7
3′-F	0.193	0.102	0.998	2.1
3′-COOH	0.149	0.106	0.999	1.9
3′-SO_3Na	0.136	0.100	0.991	1.8
3′-NO_2	0.159	0.075	0.995	1.8
Diethylaminoazobenzene derivatives				
H	—0.532	0.104	0.995	0.39
4′-CH_3	—0.715	0.128	0.997	0.27
4′-OCH_3	—	—	—	0.04
4′-F	—0.982	0.125	0.998	0.15
4′-Br	—0.724	0.100	0.995	0.25
4′-SO_2NH_2	—0.129	0.090	0.996	0.95
4′-CN	—0.006	0.099	0.992	1.30
4′-NO_2	+0.019	0.076	0.999	1.29
4′-$COCH_3$	—0.287	0.089	0.997	0.66
3′-OCH_3	—0.670	0.116	0.994	0.29
3′-Cl	—0.673	0.123	0.999	0.30
3′NO_2	—0.703	0.097	0.996	0.26

The simultaneous use in the correlation of values of σ^+ for electron-donor substituents and of σ^- for electron-acceptor substituents is explained by the presence of two reactive centres of opposite character—+C (amino-group) and –C (azo-group)—in the molecules of *p*-aminoazo-compounds. Electron-donor substituents (D) may undergo conjugation with the azo-group, and electron-acceptor substituents (A) with the amino-group:



This hypothesis explains several peculiarities of the behaviour of *p*-aminoazo-compounds containing strong –C substituents at position 4′[125,133,146]. Such compounds also exhibit an enhanced tendency to association both in solution[132,146] and in the gas phase[158].

The above effects of substituents on the (XLI) ⇌ (XLII) tautomeric equilibrium are consistent with calculations by the Hückel molecular-orbital method. Pullman and Baudel[161,162] showed that the proportion of a tautomer in the mixture varies directly with the electron density on the corresponding reactive centre. An attempt to assess separately conjugation and inductive effects on the tautomeric equilibrium has shown[129] that the π-electron densities on the reactive centres, and also the differences in delocalisation energies of the tautomers, are relatively insensitive to the inductive effect of the substituents, and also to the presence of substituents in the 3′ position.

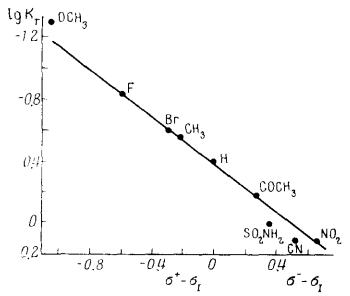


Figure 3. Dependence of $\lg K_T$ of 4′-substituted diethylaminoazobenzenes on $\sigma^+ - \sigma_I$ for electron-donor substituents and $\sigma^- - \sigma_I$ for electron-acceptor substituents[160].

The tautomeric equilibrium in acid solutions of *p*-aminoazo-compounds has been investigated quantitatively also by means of the proton magnetic resonance spectra[163]. The model compound used was 4-dimethylamino-3-methyl-3′-nitroazobenzene, which was assumed to add a proton solely at the amino-group. The calculation was based on the chemical shifts of the 2,6- and 3,5-protons and also on the position of the signal due to the *N*-methyl group. The results agree qualitatively with the above spectrophotometric data. This method could not be extended to a wide range of compounds owing to the relative inaccuracy (10–20%) of the constants obtained from the proton magnetic resonance spectra and to the inadequate solubility of the compounds.

Determination of the tautomeric equilibrium constants from the absorption spectra of solutions of *p*-aminoazo-compounds in different acid concentrations[154-156] has shown that $\lg K_T$ for the (XLI) ⇌ (XLII) equilibrium varies linearly[95,156,157] with the acidity function of the solution:

$$\lg K_T = a + b \cdot H_0 \qquad (18)$$

Parameters in Eqn. (18) are given in Table 4 for several *p*-aminoazo-compounds.

The dependence of the position of tautomeric equilibrium on the acid concentration of the solution is explained by the fact that the tautomers (XLI) and (XLII) belong to different chemical classes. Therefore their activity coefficients $f_{(XLI)}$ and $f_{(XLII)}$ vary differently with change in the properties of the medium, which in turn leads to a change in the concentration constant found for the tautomeric equilibrium:

$$K_T = K_T^* \frac{f_{XLII}}{f_{XLI}} = \frac{K_2^*}{K_1^*} \frac{f_{XLII}}{f_{XLI}} \qquad (19)$$

in which K_T* is the thermodynamic tautomeric equilibrium constant. Since K_T* is related to the thermodynamic constants K_1* and K_2* of the equilibria (XL) + H^+ ⇌ (XLI) and (XL) + H^+ ⇌ (XLII), we can express K_1* and K_2* in terms of the concentrations and the activity coefficients of the species involved in the equilibrium, substitute in Eqn. (19), take logarithms, and rearrange to obtain

$$\lg K_T^* = \lg \frac{[XLI]}{[XLII]} + \lg \frac{[H^+] \cdot f_{H^+} \cdot f_{(XL)}}{f_{XLII}} - \lg \frac{[H^+] \cdot f_{H^+} \cdot f_{XL}}{f_{XLI}} \qquad (20)$$

As

$$f_{H^+} \cdot [H^+] = a_{H^+} \qquad (21)$$

we can write from the definition of acidity function[164]

$$-\lg \left(a_{H^+} \cdot \frac{f_{XL}}{f_{XLII}} \right) = H_0' \qquad (22)$$

$$-\lg \left(a_{H^+} \cdot \frac{f_{XL}}{f_{XLI}} \right) = H_0 \qquad (23)$$

where H_0 and H_0' are acidity functions based on indicators which are respectively azo-compounds and aniline derivatives. Substituting (22) and (23) in (20) and rearranging, we obtain

$$\lg K_T = \lg K_T^* + (H_0 - H_0') \qquad (24)$$

Most acidity functions vary linearly with the normality of the acid in the range employed (3–20 *N*). Therefore Eqn. (18) follows directly from (24). Furthermore, $\lg K_T$ is a linear function of the acid normality[165].

The dependence of the position of tautomeric equilibrium on the acid concentration of the solution established for *p*-aminoazo-compounds, and also the linear relation between $\lg K_T$ and the normality and acidity function of the solution, should apply generally to any prototropic (or other) equilibria involving reactive centres of different chemical types. The slope of the relation (18) will then depend on the difference $H_0 - H_0'$ in Eqn. (24). This conclusion is not, of course, valid for the equilibrium (XXV) ⇌ (XXVI), for the reactive centres in these species are of different types.

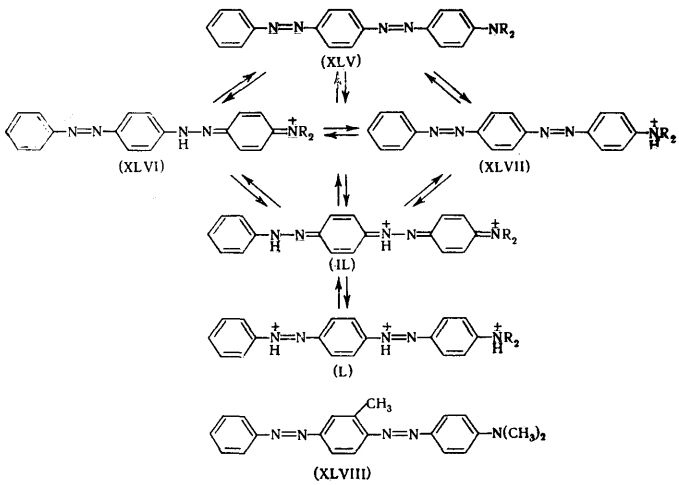
Since the basic strengths of primary and tertiary aromatic amines are described by different acidity functions[166], different values of the coefficient *b* in Eqn. (18) apply to aminoazobenzene and its derivatives and to derivatives of dimethyl- and diethyl-aminoazobenzenes (Table 4). The mean value for the latter is[95] $b = 0.103$: i.e. increase in the acidity function of the solution by unity on the H_0 scale is accompanied by an average increase of about 30% in the value of K_T for dimethyl- and diethyl-aminoazobenzene derivatives. This is probably the reason for the difference in the values obtained for K_T (Table 3) spectrophotometrically by Jaffé and from pK_{a_2} values determined at higher acid concentrations. The close similarity in the coefficients *b* in Eqn. (18) for derivatives of dimethyl- and diethyl-aminoazobenzene is apparent also in their conforming to Kabachnik's formula[167]

$$pK_{T_1} = pK_{T_2} + \text{const} \qquad (25)$$

relating the positions of tautomeric equilibrium in different solvents[156,157]. In this case K_{T_1} and K_{T_2} pertain to solutions of different acid concentrations.

The position of tautomeric equilibrium in the conjugate acids of *p*-aminoazo-compounds is influenced by additions of various salts and also by the ionic strength of the solution[146,168]. This effect has been explained by variation in the strength of hydrogen bonds between the azo-compounds and water molecules[168], and also by association phenomena[146]. However, a more probable reason is variation in the acidity of the medium on addition of the salts[169].

The electron density of the azo-group in *p*-aminoazo-compounds is increased in an excited state[170], so that the tautomeric equilibrium should be completely displaced to the quinone hydrazone tautomer ($K_T \simeq 10^{26}$).[171]



Amino-derivatives of bisphenylazobenzene (XLV), which contain five potential centres of basicity, form a special class of *p*-aminoazo-compounds. Spectrophotometric investigations[172,173] show that addition of the first proton to (XLV) yields a mixture of tautomeric cations (XLVI) and (XLVII) (λ_{max} = 540 and 355 nm). Addition of the proton to the β-nitrogen of the azo-group is proved by the marked displacement of the tautomeric equilibrium towards the ammonium tautomer on passing to 2′-methyl-4′-phenylazo-4-dimethylaminoazobenzene (XLVIII), in which the β-nitrogen atom is shielded by the methyl group.

Addition of a second proton (in 11–22 *N* sulphuric acid) is accompanied by a considerable deepening of the colour of the solution (λ_{max} = 630 nm), owing to formation of a doubly charged cation (XLIX). No other tautomeric forms are detected in these solutions. Finally, a triply charged cation (L) (λ_{max} = 500 nm) is formed in concentrated sulphuric acid. All the above characteristics of *p*-aminoazobenzene derivatives apply to the equilibrium (XLVI) ⇌ (XLVII)[173].

Aminoazo-compounds form complexes with Lewis acids[106,174-177], whose absorption spectra are completely analogous to those of acid solutions of *p*-aminoazo-compounds. From this Gutmann and Steininger concluded[106] that a mixture of two tautomeric forms is also formed on interaction with Lewis acids.

Prototropic tautomeric transitions involving the azo-group have been reported for *p*-aminoazo-compounds of the naphthalene series[131], various *N*-substituted aminoazobenzenes[111,142,178], and also amino-derivatives of phenylazoazulene[179].

REFERENCES

1. K. Venkataraman, "Chemistry of Synthetic Dyes" (Translated into Russian), Vol. 1, Goskhimizdat, 1956.
2. A. Hantzsch and A. Burawoy, Ber., 63, 1760 (1930).
3. R. Kuhn and F. Bär, Annalen, 516, 143 (1935).
4. E. J. Haselbach, Diss., Techn. Hochschule, Zürich, (1967).
5. H. Zollinger, "Chemie der Azofarbstoffe" (Translated into Russian), Goskhimizdat, Leningrad, 1960.
6. G. E. Lewis, Tetrahedron, 10, 129 (1960).
7. T. Zincke and H. Bindewald, Ber., 17, 3026 (1884).
8. J. T. Newitt and H. A. Phillips, J. Chem. Soc., 79, 160 (1901).
9. H. E. Fierz-David, L. Blangey, and H. Streif, Helv. Chim. Acta, 29, 1718 (1946).
10. J. N. Ospensen, Acta Chem. Scand., 4, 1351 (1950).
11. J. N. Ospensen, Acta Chem. Scand., 5, 491 (1951).
12. J. B. Müller, L. Blangey, and H. E. Fierz-David, Helv. Chim. Acta, 35, 2579 (1952).
13. A. Burawoy, A. G. Salem, and A. R. Thompson, J. Chem. Soc., 4793 (1952).
14. A. Burawoy and A. R. Thompson, J. Chem. Soc., 1443 (1953).
15. D. Hadzi, J. Chem. Soc., 2143 (1956).
16. G. M. Badger and R. C. Buttery, J. Chem. Soc., 614 (1956).
17. E. Sawicki, J. Org. Chem., 22, 743 (1957).
18. E. Fischer and Y. F. Frei, J. Chem. Soc., 3159 (1959).
19. G. Gabor, Y. Frei, D. Gagiou, M. Kaganowitch, and E. Fischer, Israel J. Chem., 5, 193 (1967).
20. L. Skulski and T. Urbanski, Bull. Acad. polon. Sci., Ser. Sci. chim., 8, 569 (1960).
21. Y. Yagi, Bull. Chem. Soc. Japan, 37, 1875 (1964).
22. W. R. Brode and L. E. Herdle, J. Org. Chem., 6, 713 (1941).
23. J. Schreiber, J. Socha, and K. Rotschein, Coll. Czech. Chem. Comm., 35, 857 (1970).
24. G. Oddo and E. Puxeddu, Gazzetta, 36, II, 1 (1906).
25. S. B. Hendricks, O. R. Wulf, G. E. Hilbert, and U. Liddel, J. Amer. Chem. Soc., 58, 1991 (1936).
26. K. J. Morgan, J. Chem. Soc., 2151 (1961).
27. K. Ueno, J. Amer. Chem. Soc., 79, 3066 (1957).
28. G. D. Bagratishvili, Trudy Inst. Khim. Melikishvili Akad. Nauk Gruz. SSR, 14, 89 (1958).
29. L. A. Gribov, Yu. M. Dedkov, and A. V. Kotov, Teor. Eksper. Khim., 4, 316 (1968).
30. B. I. Stepanov, B. A. Korolev, and S. L. Polyakova, Zhur. Obshch. Khim., 37, 2138 (1967).
31. J. Socha, J. Horska, and M. Večera, Coll. Czech. Chem. Comm., 34, 2982 (1969).
32. D. N. Shigorin, I. Ya. Pavlenishvili, and V. I. Kokachashvili, Zhur. Fiz. Khim., 40, 3006 (1966) [Russ. J. Phys. Chem., No. 12 (1966)].
33. D. N. Shigorin, in "Vodorodnaya Svyaz'" (The Hydrogen Bond), Nauka, Moscow, 1964, p. 198.
34. M. Dolinsky and J. H. Jones, J. Assoc. Offic. Agric. Chemists, 37, 197 (1954).
35. L. Sculsci, Bull. Acad. polon. Sci., Ser. Sci. chim., 14, 37 (1966).
36. G. D. Bagratishvili, Soobshch. Akad. Nauk Gruz. SSR, 17, 615 (1956).
37. B. I. Stepanov and B. A. Korolev, Zhur. Obshch. Khim., 38, 1365 (1968).
38. B. I. Stepanov and B. A. Korolev, Zhur. Org. Khim., 5, 1673 (1969).

39. A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, J. Chem. Soc. (B), 1308 (1968).
40. B. L. Kaul, P. M. Nair, and A. V. R. Rao, Tetrahedron Letters, 3897 (1966).
41. L. W. Reeves, Canad. J. Chem., 38, 748 (1960).
42. I. F. Vladimirtsev and I. Ya. Postovskii, Zhur. Fiz. Khim., 31, 432 (1957).
43. I. Ya. Postovskii and I. F. Vladimirtsev, Dokl. Akad. Nauk SSSR, 83, 855 (1952).
44. C. H. Giles and J. A. Grant, J. Soc. Dyers and Colourists, 84, 432 (1968).
45. H. Rau, Z. Naturforsch., 24b, 494 (1969).
46. H. Rau, Ber. Bunsenges, phys. Chem., 73, 810 (1969).
47. V. Bekarek, K. Rothschein, P. Vetešnik, and M. Večera, Tetrahedron Letters, 3711 (1968).
48. V. Bekarek, J. Dobas, J. Socha, P. Wetešnik, and M. Večera, Coll. Czech. Chem. Comm., 35, 1406 (1970).
49. H. Rau, Ber. Bunsenges. phys. Chem., 72, 637 (1968).
50. E. Fischer, Fortschr. chem. Forsch., 7, 605 (1967).
51. J. Schreiber and M. Večera, Coll. Czech. Chem. Comm., 34, 2145 (1969).
52. H. E. Fierz-David, L. Blangey, and E. Merian, Helv. Chim. Acta, 34, 846 (1951).
53. D. Samuel and E. Fischer, Ber. Bunsenges. phys. Chem., 69, 155 (1965).
54. G. Gabor and E. Fischer, J. Phys. Chem., 66, 2478 (1962).
55. V. V. Perekalin and Z. S. Segalina, Zhur. Obshch. Khim., 24, 683 (1954).
56. S. Millefiori and F. Guerrera, Ricerca sci., 39, 612 (1969).
57. A. Burawoy and J. Chamberlain, J. Chem. Soc., 3734 (1952).
58. L. Skulski, Bull. Acad. polon. Sci., Ser. Sci. chim., 14, 29 (1966).
59. W. R. Brode, L. Verne, and E. Cheyney, J. Org. Chem., 6, 341 (1941).
60. A. G. Catchpole, W. B. Foster, and R. S. Holden, Spectrochim. Acta, 18, 1353 (1962).
61. G. Wettermark, M. E. Langmuir, and D. G. Anderson, J. Amer. Chem. Soc., 87, 476 (1965).
62. G. Gabor, J. F. Frei, and E. Fischer, J. Phys. Chem., 72, 3266 (1968).
63. W. Borsche, W. Müller, and C. A. Bodenstein, Annalen, 472, 201 (1929).
64. W. Lauer and S. Miller, J. Amer. Chem. Soc., 57, 520 (1935).
65. L. S. Geidysh, G. A. Nikoforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1045 (1970).
66. V. V. Ershov and G. A. Nikoforov, Uspekhi Khim., 35, 1953 (1966) [Russ. Chem. Rev., No. 11 (1966)].
67. I. Ya. Bershtein and Yu. L. Kaminskii, Optika i Spektrosk., 15, 705 (1964).
68. H. H. Jaffé and Si-Yung Yeh, J. Amer. Chem. Soc., 81, 3279 (1959).
69. Ch. S. Frankovskii and N. V. Melamed, Zhur. Org. Khim., 5, 108 (1969).
70. W. Strachan, A. Dolenko, and A. Buncel, Canad. J. Chem., 47, 3631 (1969).
71. L. Skulski and T. Urbanski, Bull. Acad. polon. Sci., Ser. Sci. chim., 8, 561 (1960).
72. F. Kaufler and W. Suchanek, Ber., 40, 518 (1907).
73. S. S. Joshi, D. S. Deorha, and P. C. Joshi, J. Indian Chem. Soc., 38, 395 (1961).
74. C. H. Giles and E. L. Neustädter, J. Chem. Soc., 1864 (1952).
75. Yu. M. Dedkov and A. V. Kotov, Izv. Akad. Nauk. SSSR, Ser. Khim., 1161 (1969).
76. P. Ramart-Lucas, T. Guilmart, and M. Martynoff, Bull. Soc. chim. France, 415 (1947).
77. L. Skulski and T. Urbanski, Roczniki Chem., 36, 801 (1962).
78. M. Martynoff, Compt. rend., 236, 87 (1953).
79. M. A. Chekalin and N. A. Zhukova, Zhur. Prikl. Spektrosk., 10, 1008 (1969).
80. W. R. Brode and D. R. Eberhart, J. Org. Chem., 5, 157 (1940).
81. G. D. Bagratishvili, Dokl. Akad. Nauk SSSR, 96, 753 (1954).
82. M. A. Chekalin and N. A. Zhukova, Zhur. Org. Khim., 3, 908 (1967).
83. D. A. Ibbitson, P. S. James, and R. A. Knaust, J. Chem. Soc., 5163 (1961).
84. A. G. Catchpole and R. A. Knaust, J. Chem. Soc., 4241 (1960).
85. S. F. Filippychev, Dokl. Akad. Nauk SSSR, 73, 731 (1950).
86. Yu. N. Sheinker, E. M. Peresleni, N. P. Zosimova, and Yu. I. Pomerantsev, Zhur. Fiz. Khim., 33, 2096 (1959) [Russ. J. Phys. Chem., No. 9 (1959)].
87. A. Hantzsch and F. Hilscher, Ber., 41, 1171 (1908).
88. F. Kehrmann, Ber., 48, 1933 (1915).
89. F. Kehrmann and S. Hempel, Ber., 50, 856 (1917).
90. C. Gustafson, Suomen Kem., 18B, 11 (1945).
91. H. H. Jaffé and R. W. Gardner, J. Amer. Chem. Soc., 80, 319 (1958).
92. M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov, and T. A. Melent'eva, Dokl. Akad. Nauk SSSR, 124, 1061 (1959).
93. M. I. Kabachnik, Zhur. Vses. Khim. Obshch. Mendeleeva, 7, 263 (1962).
94. H. H. Jaffé and H. L. Jones, Adv. Heterocyclic Chem., 4, 209 (1965).
95. I. Ya. Bershtein and O. F. Ginzburg, Reakts. Spos. Org. Soed., 5, 690 (1968).
96. F. Gerson and E. Heilbronner, Helv. Chim. Acta, 42, 1877 (1959).
97. A. Saupe, Z. Naturforsch., 18a, 336 (1963).
98. H. H. Jaffé, Si-Yung Yeh, and R. W. Gardner, J. Mol. Spectroscopy, 2, 120 (1958).
99. G. E. Lewis, J. Org. Chem., 25, 2193 (1960).
100. F. Gerson, E. Heilbronner, A. van Veen, and B. M. Wepster, Helv. Chim. Acta, 43, 1889 (1960).
101. E. Haselbach and E. Heilbronner, Tetrahedron Letters, 4531 (1967).
102. J. Weinstein and E. McIninch, J. Amer. Chem. Soc., 82, 6064 (1960).
103. H. H. Jaffé, Chem. Rev., 53, 191 (1953).
104. G. A. Eian and C. A. Kingsbury, Bull. Chem. Soc. Japan, 43, 739 (1970).
105. M. A. Hoefnagel, A. Van-Veen, and B. M. Wepster, Rec. Trav. chim., 88, 562 (1969).
106. V. Gutmann and A. Steininger, Monatsh., 96, 1173 (1965).
107. J. H. Collins and H. H. Jaffé, J. Amer. Chem. Soc., 84, 4708 (1962).
108. G. S. Hampson and J. M. Robertson, J. Chem. Soc., 409 (1941).
109. G. Cilento, J. Org. Chem., 24, 2015 (1959).
110. F. Gerson and E. Heilbronner, Helv. Chim. Acta, 45, 51 (1962).
111. L. M. Yagupol'skii and L. Z. Gandel'sman, Zhur. Obshch. Khim., 35, 1252 (1965).
112. W. Michler, Ber., 11, 1944 (1878).

113. J. Thiole, Ber., 36, 3965 (1903).
114. G. D. Bagratishvili, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1954.
115. K. Auwers, Ber., 33, 1314 (1900).
116. G. M. Badger, R. G. Buttery, and G. E. Lewis, J. Chem. Soc., 1888 (1954).
117. E. Sawicki, J. Org. Chem., 22, 1084 (1957).
118. G. Cilento, E. C. Miller, and J. A. Miller, J. Amer. Chem. Soc., 78, 1718 (1956).
119. A. J. Ryan, Tetrahedron, 20, 1547 (1964).
120. I. M. Klotz, H. A. Friess, J. Y. Chen Ho, and M. Mellody, J. Amer. Chem. Soc., 76, 5136 (1954).
121. W. S. McGuire, T. F. Izzo, and S. Zuffanti, J. Org. Chem., 21, 632 (1956).
122. H. H. Jaffé, J. Chem. Phys., 21, 415 (1953).
123. L. Pentimalli, Tetrahedron, 5, 27 (1959).
124. C. R. Bury, J. Amer. Chem. Soc., 57, 2115 (1935).
125. M. T. Rogers, T. W. Campbell, and R. W. Maatman, J. Amer. Chem. Soc., 73, 5122 (1951).
126. Si-Yung Yeh and H. H. Jaffé, J. Amer. Chem. Soc., 81, 3283 (1959).
127. E. Sawicki, J. Org. Chem., 22, 365 (1957).
128. Yu. A. Zhdanov and V. I. Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Organic Chemistry), Izd. Rostovsk. Univ., Rostov, 1966, p. 117.
129. I. Ya. Bershtein and V. I. Minkin, Zhur. Org. Khim., 5, 2207 (1969).
130. I. Ya. Bershtein and O. F. Ginzburg, Zhur. Org. Khim., 3, 2032 (1967).
131. E. Sawicki, J. Org. Chem., 22, 621 (1957).
132. A. Zenhäusern and H. Zollinger, Helv. Chim. Acta, 45, 1882 (1962).
133. M. Isaks and H. H. Jaffé, J. Amer. Chem. Soc., 86, 2209 (1964).
134. T. Jasinski and T. Skarzynska-Klentak, Roczniki Chem., 44, 657 (1970).
135. T. Jasinski and T. Skarzynska-Klentak, Roczniki Chem., 44, 1081 (1970).
136. Yu. L. Khaldna and V. A. Pal'm, Dokl. Akad. Nauk SSSR, 135, 667 (1960).
137. Yu. L. Khaldna, Reakts. Spos. Org. Soed., 5, 525 (1968).
138. Y. Tanizaki, T. Kobayashi, and T. Hoshi, Bull. Chem. Soc. Japan, 39, 558 (1966).
139. R. Titeica, G. Palade, G. Banateanu, and A. Strugaru, Bull. Inst. petrol. gase si geol., 9, 189 (1963).
140. D. Vorländer, Ber., 37, 1648 (1904).
141. E. E. Milliaresi and V. A. Izmail'skii, Zhur. Obshch. Khim., 32, 3451 (1962).
142. W. C. J. Ross and G. P. Warwick, J. Chem. Soc., 1719 (1956).
143. F. Gerson and E. Heilbronner, Helv. Chim. Acta, 45, 42 (1962).
144. I. N. Zhmurova, Zhur. Obshch. Khim., 27, 2704 (1957).
145. L. Horner and H. Müller, Chem. Ber., 89, 2756 (1956).
146. A. Zenhäusern and H. Zollinger, Helv. Chim. Acta, 45, 1890 (1962).
147. E. Sawicki, J. Org. Chem., 21, 605 (1956).
148. A. I. Kipriyanov and I. N. Zhmurova, Zhur. Obshch. Khim., 23, 626 (1953).
149. H. H. Jaffé and Si-Yung Yeh, J. Org. Chem., 22, 1281 (1957).
150. H. H. Jaffé and A. L. Miller, Tetrahedron Letters, 1489 (1966).
151. M. Isaks, Diss. Abs., 24, 4998 (1964).
152. H. H. Jaffé and A. L. Miller, Reakts. Spos. Org. Soed., 2, No. 4 (6), 177 (1965).
153. R. L. Reeves, J. Amer. Chem. Soc., 88, 2240 (1966).
154. Yu. L. Kaminskii, I. Ya. Bershtein, and O. F. Ginzburg, Dokl. Akad. Nauk SSSR, 145, 330 (1962).
155. Yu. L. Kaminskii and I. Ya. Bershtein, in "Trudy Konferentsii po Problemam Primeneniya Korrelyatsionnykh Uravnenii v Organicheskoi Khimii" (Proceedings of a Conference on Problems in the Application of Correlation Equations to Organic Chemistry), Tartu, 1962, Vol. 1, p. 333.
156. I. Ya. Bershtein and O. F. Ginzburg, Zhur. Org. Khim., 4, 1260 (1968).
157. I. Ya. Bershtein and O. F. Ginzburg, Dokl. Akad. Nauk SSSR, 180, 98 (1968).
158. H. S. Green, F. Jones, M. Syz, and H. Zollinger, Helv. Chim. Acta, 48, 386 (1965).
159. Si-Yung Yeh and H. H. Jaffé, J. Amer. Chem. Soc., 81, 3274 (1959).
160. I. Ya. Bershtein, Candidate's Thesis, Lensovet Leningrad Institute of Technology, Leningrad, 1968.
161. B. Pullman and J. Baude, Compt. rend., 238, 2529 (1954).
162. A. Pullman and B. Pullman, Compt. rend., 243, 1322 (1956).
163. J. Grénacher, H. Suhr, and A. Zenhäusern, Helv. Chim. Acta, 44, 313 (1961).
164. M. A. Paul and F. A. Long, Chem. Rev., 57, 1 (1957).
165. Yu. L. Kaminskii and I. Ya. Bershtein, see Ref. 155, p. 338.
166. E. M. Arnett and G. W. Mach, J. Amer. Chem. Soc., 88, 1177 (1966).
167. M. I. Kabachnik, Dokl. Akad. Nauk SSSR, 83, 407 (1952).
168. V. V. Pal'chevskii, L. A. Polyanskaya, E. M. Semenova, and E. E. Yudovich, Optika i Spektrosk., 26, 1031 (1969).
169. A. Ferse and E. Ferse, Z. Chem., 6, 241 (1966).
170. D. L. Beveridge and H. H. Jaffé, J. Amer. Chem. Soc., 88, 1948 (1966).
171. R. H. Ellerhorst, H. H. Jaffé, and A. L. Miller, J. Amer. Chem. Soc., 88, 5342 (1966).
172. E. Sawicki, J. Org. Chem., 23, 532 (1958).
173. I. Ya. Bershtein and O. F. Ginzburg, Zhur. Org. Khim., in the press.
174. G. E. Lewis, J. Franklin Inst., 226, 293 (1938).
175. F. Feigl and G. R. Heisig, J. Amer. Chem. Soc., 73, 5631 (1951).
176. R. J. Shuba and S. T. Zenchelsky, J. Amer. Chem. Soc., 82, 4136 (1960).
177. N. B. Kupletskaya, N. N. Delyagin, V. A. Ptitsyna, A. V. Upadysheva, L. A. Kazitsina, and O. A. Reutov, Zhur. Org. Khim., 3, 1537 (1967).
178. J. A. Richetts and C. S. Cho, J. Org. Chem., 26, 2125 (1961).
179. F. Gerson, Helv. Chim. Acta, 46, 1109 (1963).

Leningrad Scientific Research Institute
of Antibiotics