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The Crystal Structures of Potentially Tautomeric Compounds

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Data on the structures of potentially proto-, metallo-, and carbono-tropic compounds, obtained mainly by X-ray diffraction, are surveyed. The results of neutron and electron diffraction studies have also been partly used. It is shown that a characteristic feature of all the systems considered is the formation of hydrogen or secondary bonds ensuring the contribution of both possible tautomeric forms to the structure. Systematic consideration of the experimental data leads to the conclusion that there is a close relation between the crystal structure and the dynamic behaviour of the molecules in solution and that secondary and hydrogen bonds play a significant role in the tautomeric transition.
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I. INTRODUCTION

Among the physical methods for the investigation of molecular structure, X-ray diffraction analysis, which makes it possible to determine the structure objectively without any *a priori* models, occupies the principal place. Systematic consideration of the enormous amount of experimental data obtained by this method shows that in the crystals of the vast majority of organic and organometallic compounds the distances between atoms of the given kind can be divided into two groups: the distances between atoms joined by a chemical bond (they are characterised by the sum of the covalent radii) and the distances between atoms not linked by chemical bonds, the shortest of which are usually close to the sums of the van der Waals radii. Since the van der Waals radii are greater by ~0.8 Å than in the covalent radii, in the spectrum of interatomic distances there is a "gap" separating valence distances from non-valence distances.

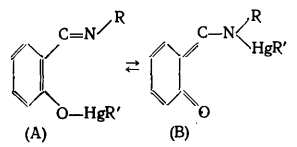
However, in the last few years an increasing number of interatomic distances occupying precisely this gap have been observed. The accumulation of experimental data on structures of this type suggests the possibility of applying X-ray diffraction not only to the determination of the geometrical characteristics of the initial substances and reaction products but also to the solution of certain problems concerning chemical processes. This field is undergoing an increasing development at the present time. In particular, systematic studies are being prosecuted in Switzerland in Bürgi's group[1]. Burgi believes that any chemical reaction involving the dissociation of some bond and the formation of others should be characterised by structural data demonstrating a continuous transition between the covalent bond and the van der Waals contact.

Bürgi and coworkers carried out X-ray diffraction studies on a series of alkaloids and related compounds containing a tertiary amino-group and a carbonyl group. A set of these structures, in which a correlation has been found between the shortening of the intramolecular N...C contact and the breakdown of the coplanarity of the covalent bonds involving the C atom, constitutes a model of the nucleophilic addition to the carbonyl group involving the formation of an intermediate with a tetrahedral carbon atom. An analogous correlation has also been observed for the O...C=O contacts[2].

This review deals with the application of X-ray diffraction analysis to the study of elemento- and proto-tropic systems.

II. DERIVATIVES OF SALICYLALDEHYDE

In the determination of the crystal structures of tautomeric (or potentially tautomeric) compounds the problem of which of the two possible molecular forms exist in the crystal arises in the first place. Thus Minkin and coworkers demonstrated[3] by electronic absorption and luminescence spectroscopy that phenyl- and methylmercury derivatives of *o*-hydroxyarylaldimines exist in solution in the form of an equilibrium mixture of benzenoid and quinonoid tautomers, whose ratio varies with temperature and solvent polarity:



X-Ray diffraction analysis showed[4] that in the crystal the phenylmercury *N*-methylsilicylideneaminate molecule is an *N*-derivative with the *cis*-configuration relative to the C(2)–C(3) exocyclic bond (Fig.1). This configuration is favourable for intramolecular coordination and the Hg...O distance [2.44 (3) Å] in this molecule is indeed smaller by ~0.5 Å than the sum of the van der Waals radii of these atoms, which indicates a coordination interaction (a secondary Hg...O bond). Coordination leads to the breakdown of the linearity of the N–Hg–C fragment: the angle between the covalent bonds involving the Hg atom is 167(1)°.

The detection of the Hg–N covalent bond, which has the usual length, implies that the molecular structure is best described in terms of the quinonoid form B, but the strong

intramolecular Hg...O interaction indicates a considerable contribution of the benzeneoid structure A also. The interatomic distances in the salicylideneaminate ligand can therefore be intermediate between the distances in A and B, but the accuracy with which the location of the carbon atoms can be specified in the presence of a heavy metal such as mercury is insufficient for the consideration of such fine structural details.

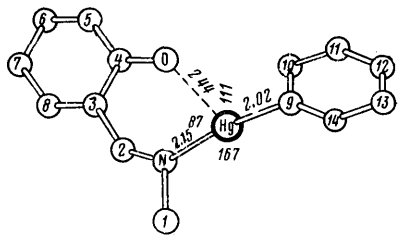


Figure 1.

In contrast to this structure, in the dimethyltin *N*-(2-hydroxyphenyl)salicylideneaminate molecule[5] the Sn...O distance in the salicylideneaminate chelate ring [2.130(7) Å] is somewhat shorter than the Sn–N distance [2.225(8) Å], which indicates that the benzenoid *O*-form predominates (Fig.2). The distribution of bond lengths in this chelate ring is also consistent with the above treatment. At the same time, the shortening of the C–O bond to 1.30(1) Å compared with the C–O bond in the hydroxyphenyl fragment of the same molecule [1.35(1) Å] and with the value usual for phenols (1.38 Å) as well as the shortening of the C–C(=N) bond to 1.45(1) Å indicate a contribution of the quinonoid *N*-form.

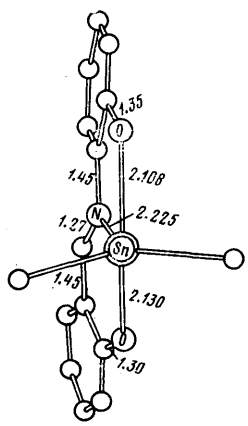


Figure 2.

In *N*,*N'*-ethylenebis-salicylideneaniline[6] (Fig.3) and *N*-*N'*-(*o*-phenylene)bis-salicylideneaniline[7] the salicylideneamine fragment exists in the benzenoid form, although the O–H...N intramolecular hydrogen bond, analogous to the secondary Hg...O bond in the phenylmercury derivative, ensures some contribution (albeit very small) of the quinonoid structure. In transition metal complexes the salicylideneaminate ligand has an intermediate structure, all its interatomic distances being close to the lengths of aromatic bonds (see, for example, Lingafelter and Braun[8]).

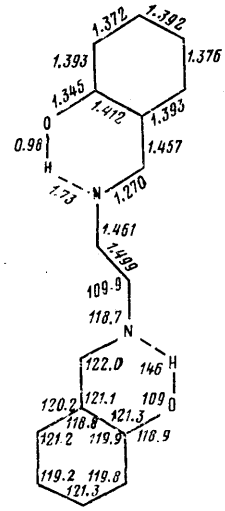


Figure 3.

The structure of the salicylaldehyde complex of diethylthallium[9] is also best described in terms of the benzenoid form: the Tl–O(1) distance involving the phenolic oxygen atom (2.46 Å) is much shorter than Tl–O(2) (2.61 Å); the C(1)–O(2) bond (1.23 Å) is close to the normal double bond and the C(2)–O(1) bond (1.32 Å) is close to a single bond.

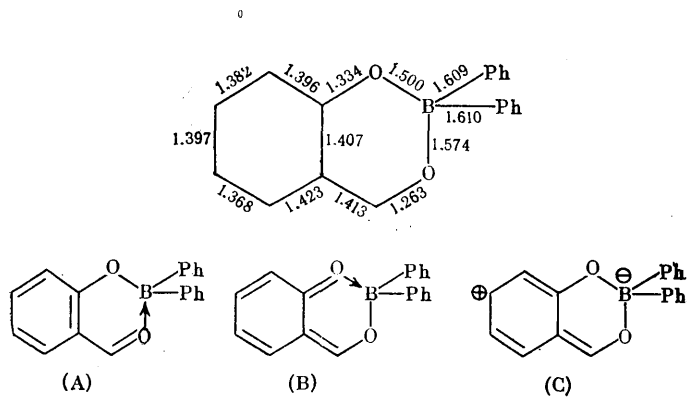


Figure 4.

The salicylaldehyde complex of diphenylboron has an analogous structure[10] (Fig.4). The B–O bond lengths in this molecule are significantly non-equivalent: 1.500 and 1.574 Å, which leads to the conclusion that the contribution of the benzenoid form A to the structure predominates, but even the shorter of these bonds is somewhat longer than

the usual value 1.477 Å. The absence of heavy atoms from this molecule made it possible to determine the structure with a higher accuracy and to discover the real distribution of bond lengths, indicating a significant contribution of the three resonance forms—benzenoid (A), *o*-quinonoid (B), and *p*-quinonoid (C)—to the structure.

A similar distribution of bond lengths has been found in the *o*-vanilline molecule[11]†, where a strong intramolecular hydrogen bond was observed (Fig.5*a*), but, judging from the C–O and C–C (exocyclic) bonds, the contribution of the benzenoid form is in this case somewhat greater than in the boron compound. The bond lengths in the aldehyde group are significantly different from the corresponding values in 2-nitrobenzaldehyde[13] (Fig.5*b*), where there is no hydrogen bond. Similar structures are characteristic also of the salicylic acid molecule (determined by X-ray diffraction[14] and neutron diffraction[15]) and the 2-amino-3-methylbenzoic acid molecule[16].

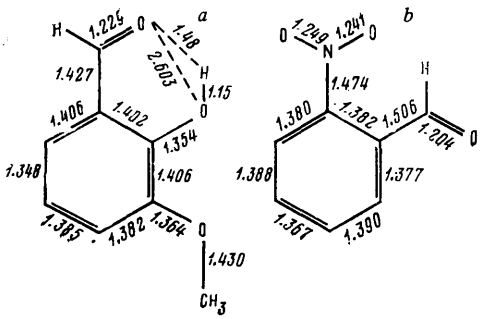


Figure 5.

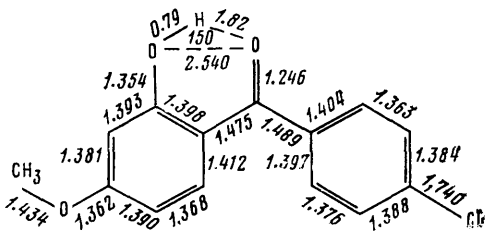


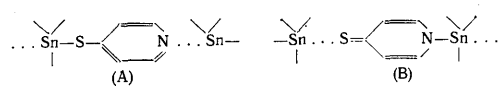
Figure 6.

The quinoid form makes a significant contribution to the structures of 2-hydroxy-4-methoxybenzophenone[17] and 4-chloro-2-hydroxy-4'-methoxybenzophenone[18] (Fig.6), where a six-membered ring is also formed as a result of an intramolecular hydrogen bond. In the 2,4-dihydroxybenzophenone crystal[19] there is an intermolecular as well as an intramolecular hydrogen bond, so that both the *o*-quinonoid and *p*-quinonoid forms should contribute to the resultant structure. As a result of this, although the C=O, C–O, and C–C (exocyclic) bonds are similar in all three structures, in the benzene ring of the last structure only one bond is distinctly shortened, namely that which should be double in both *o*- and *p*-quinonoid structures.

†The structure of the unsubstituted salicylaldehyde was investigated only in 1953 [12] and the accuracy of its determination is insufficient for the consideration of fine structural details.

III. HYDROXY-, MERCAPTO-, AND AMINO-PYRIDINES

Potentially metallotropic compounds can also form systems with intermolecular coordination in the crystalline state. In particular, the triphenyltin derivative of 4-thiopyridone has such a structure. In principle, its structure can be described in terms of one of two forms: the mercaptopyridine form (A), or the thiopyridone form (B), or a resonance hybrid of forms (A) and (B) with equal contributions by each:



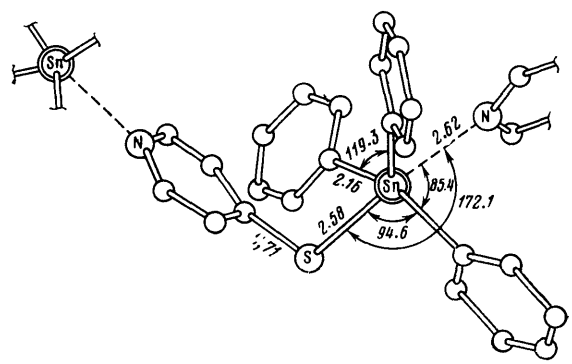


Figure 7.

X-Ray diffraction analysis showed[20] that the crystal is made up of infinite zig-zag chains (Fig.7) with trigonal-bipyramidal coordination of the tin atom. The Sn–S and Sn–N distances are longer than the corresponding single bonds but are appreciably shorter than the normal van der Waals contacts, which indicates a strong intermolecular coordination. However, the contributions of the two limiting forms to the given structure are nevertheless not the same. The Sn–S distance (2.58 Å) exceeds the length of the single bond by only 0.14 Å (the sum of the covalent radii is 2.44 Å [21]), while the Sn...N distance (2.62 Å) exceeds the single bond length by 0.52 Å (the sum of the covalent radii is 2.10 Å). Furthermore, the S–Sn–C valence angles (the average angle is 94.6°) are greater than the N...Sn–C angles (85.4°) and smaller than the ideal value for a trigonal bipyramid (90°), i.e. there is a tendency towards the retention of a tetrahedron at the Sn atom with participation of the S atom. Thus the structure of the test compound in the crystal is best described in terms of the mercaptopyridine form (A), although the contribution of form (B) is considerable. Apart from the lengthening of the Sn–S bond already mentioned, this is indicated by the shortening of the S–C bond to 1.71 Å compared with the normal value (1.78 Å). The triphenyl-lead derivative of 4-thiopyridone has a very similar structure[22].

In contrast to these compounds, which are S-derivatives in the crystal, the isothiocyanate $(CH_3)_2Sn(NCS)_2$ [23] and $(CH_3)_3SnNCS$ [24] are *N*-derivatives: their Sn–N bond lengths are respectively 2.14 and 2.15 Å, while the Sn...S distances are 3.20 and 3.13 Å.

For both salicylaldehyde and pyridone (hydroxypyridine) derivatives, a considerable similarity of the crystal structures of the metallotropic compounds and their prototropic analogues has been observed. Unfortunately, unsubstituted 4-thiopyridone has not been investigated by X-ray diffraction, but the structures of a series of 4-pyridone derivatives are known. Comparison of the structures of the 2,3,5,6-tetrachloro-derivative (I) [25] and the 3,5-dichloro-2,6-dimethyl derivative (II) [25,26] is of greatest interest. In both compound (I) and compound (II) hydrogen bonds connecting the molecules into infinite chains have been discovered, but compound (I) is a hydroxypyridine tautomer, while compound (II) is a pyridone tautomer (Fig.8).

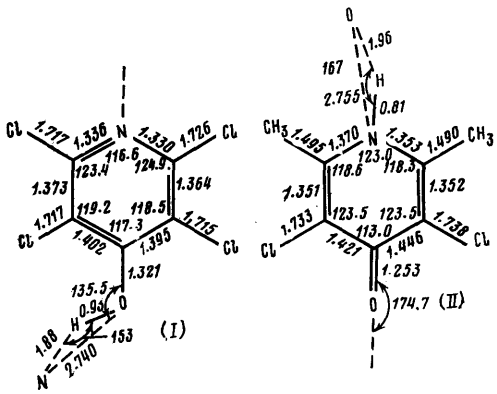


Figure 8.

The main evidence for this comes from the location of the hydrogen atoms in the two structures: the O–H...N hydrogen bond with an O–H distance of 0.93 Å, an H...N distance of 1.88 Å, and an O–H...N angle of 153° is formed in compound (I); in compound (II) the N–H...O bond has an N–H length of 0.81 Å, an H...O length of 1.96 Å, and an N–H...O angle of 167°. The lengths of the valence bonds and the angles also indicate the presence of hydroxy- and oxo-tautomers. It is known (see, for example, Singh[27]) that in six-membered heterocycles the endocyclic bond at an N atom linked to an H atom is much greater (>120°) than at an N atom not linked to an H atom (<120°), which agrees with the values observed for structures (I) and (II). Furthermore the C–O bond length in compound (II) approaches the value of 1.215 Å in aldehydes and ketones[28], while in compound (I) it is close to the value (1.36–1.38 Å) characteristic of aromatic alcohols, although the former is appreciably lengthened while the latter is actually shortened. Finally the bonds in the ring of compound (II) indicate an appreciable localisation, while in compound (I) they are close to the corresponding values for pyridine (the N–C and C–C bond lengths are 1.340 and 1.394 Å respectively[28]).

The stabilisation of the hydroxypyridine form of compound (I) is due to the presence of electron-accepting substituents in the α-position relative to the N atom: by increasing the acidity of the pyridone form and reducing the basicity of the N atom in the hydroxypyridine form, these substituents promote a shift of the tautomeric equilibrium towards the hydroxypyridine form[29]. However, one should note that, although both the intermolecular coordination involving the metal atom and the hydrogen bond lead to the generation in the crystal of forms intermediate between the two limiting forms (which is manifested particularly by the lengthening of the C=O bonds and the shortening of the C–O bonds in pyridone derivatives), the structure of the organotin derivative of 4-thiopyridone is much closer to the resonance hybrid of the two forms than all the known structures of organic analogues.

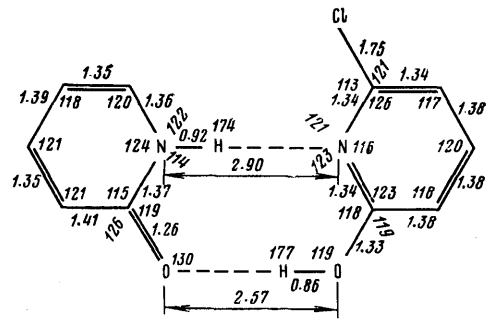


Figure 9.

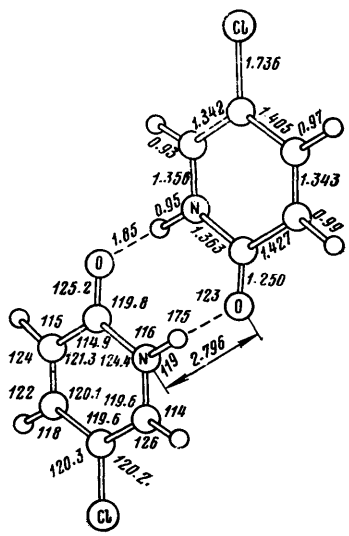


Figure 10.

A significant substituent influence on the stabilisation of a particular tautomeric form has been observed also in 2-pyridone derivatives: 2-pyridone and its 6-chloro-derivative form a molecular complex in which the unsubstituted molecule is in the pyridone form, while the substituted molecule is in the hydroxypyridine form[30] (Fig.9). α-Pyridone itself[31], 5-chloro-2-pyridone[32], α-thiopyridone[33], and 3-hydroxy-6-methyl-2-thiopyridone[34] exist in the crystal

in the pyridone form, while 6-chloro- [35] and 6-bromo-2-hydroxypyridine[36] exist in the hydroxypyridine form. In all these structures the hydrogen bonds are intermolecular. The structural unit in both the pyridone and hydroxypyridine forms is in most cases a centrosymmetric dimer (Fig.10) and only in the α-pyridone crystal have infinite helical chains been found (Fig.11). Intramolecular hydrogen bonds are not formed in these systems, since the geometrical conditions (the closure of a three-membered ring) are very unfavourable for them.

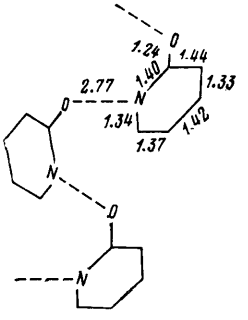
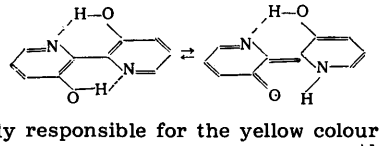


Figure 11.

However, when a hydrogen atom is replaced by a tin atom, a chelate structure becomes possible. Dichlorobis(2-pyridinethiolato)tin has such a structure[37]. In contrast to triphenyltin pyridine-4-thiolate[20] (see above), the Sn–S bonds in these molecules (with an average length of 2.464 Å) are slightly lengthened compared with the normal single bond; at the same time the Sn–N bond length (2.264 Å) also exceed the sum of the covalent radii only by 0.16 Å. This behaviour can be explained by the enhancement of the coordinating capacity of the metal atom and the enhancement of the electron-accepting properties of the substituents, which has been frequently quoted in the literature (see, for example, Furmanova et al.[38]). The distribution of bond lengths in the nucleus is intermediate between those for the mercaptopyridine and thiopyridone forms: the C–S bond lengths are 1.74 Å, the average lengths of the formally double C=C bond in the ring (for the *o*-quinonoid structure) are 1.37 Å, and the lengths of single bonds are 1.41 Å.

In hexakis(2-pyridone)copper perchlorate[39] the complex includes pyridone molecules which have retained the H atoms of their NH groups (the positions of these atoms have been determined objectively by X-ray diffraction) and accordingly exist in a distinctly pyridone form (Fig.12). A somewhat different quinonoid form contributes to the structure of 2,2′-bis-6-methyl-3-pyridinol[40] (Fig.13):



It is apparently responsible for the yellow colour of the compound. In the crystals of 2-aminopyridine[41] and 2-amino-5-chloropyridine [according to the data of Kvick and Backens[42] (X-ray diffraction) and Kvick et al.[43] (neutron diffraction)], as well as in the structures of 2-hydroxypyridine derivatives the molecules form centrosymmetric dimers via N–H...N hydrogen bonds with lengths of 3.071 and 3.058 Å. The C–NH_2 bonds in both molecules [1.351(2) and 1.357(2) Å] are shorter than in the 3-aminopyridine molecule [(1.384(4) Å] incapable of giving rise to the quinonoid form[44].

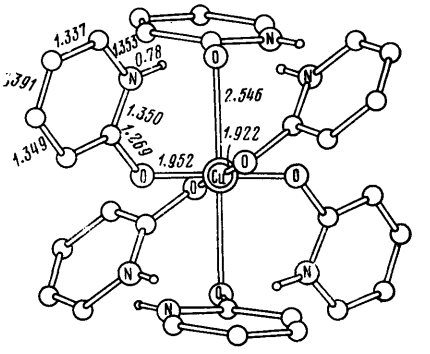


Figure 12.

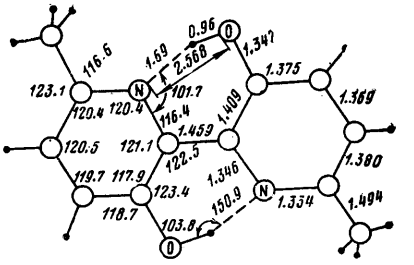


Figure 13.

IV. QUINONE OXIMES AND AMINOQUINONES

An equalised structure, which precludes a conclusion about the predominance of a particular form, obtains in the crystal of triphenyl-lead 2-fluoro-4-nitrosophenoxide[45]. The crystal is made up of infinite chains (Fig.14). The Pb atom has a trigonal-bipyramidal coordination with the O atoms in the axial positions. The difference between the Pb–O bond lengths (2.43 and 2.50 Å) is close to the error in their determination. Three Pb–C bonds are coplanar: the sum of the C–Pb–C angles is 359.9° and the average O(1)–Pb–C and O(2′)–Pb–C angles are 89.8° and 90.4°. Thus, neither the Pb–O distances nor the valence angles at the Pb atom indicate the predominance of a particular form and the structure is best described as a resonance hybrid with equal contributions by the quinone oxime and nitrosophenol forms.

Infinite chains formed via hydrogen bonds have also been found in the structure of free *p*-quinone oxime[46], but the molecule of this compound exists in the crystal as a distinct quinone oxime form (Fig.15). On the other hand, the C=N bond (1.309 Å) is longer and the N–O bond (1.374 Å) is shorter than in cyclohexane-1,4-dione dioxime (1.276 and

1.411 Å respectively[47]), although the H atom of the oxime groups of the latter molecule are also involved in the formation of hydrogen bonds. Thus a partial redistribution of the π-bonds is manifested distinctly only for the *p*-quinone oxime system capable of a tautomeric transformation.

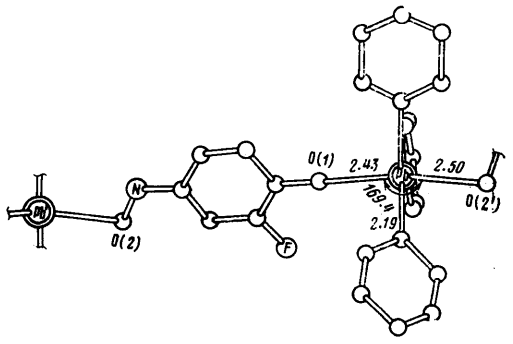


Figure 14.

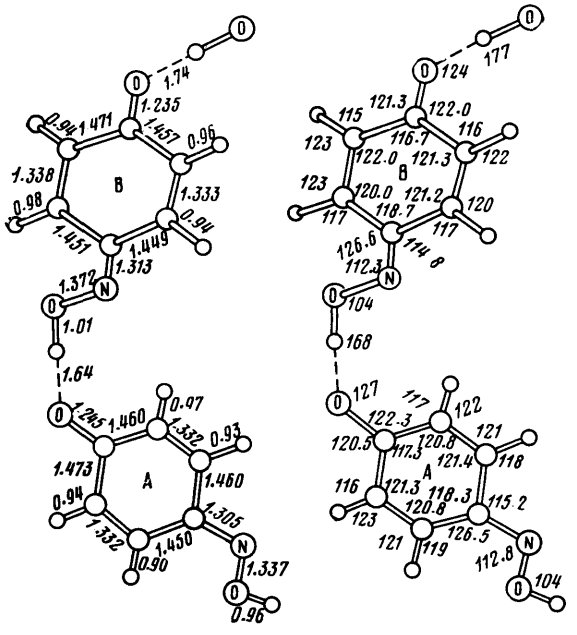


Figure 15.

6-Chloro-3-methyl-*p*-nitrosophenol, 6-bromo-3-methyl-*p*-nitrosophenol, and 3-chloro-*p*-nitrosophenol, investigated previously on the basis of projections, have similar structures[48,49]. It would be of interest to compare the structures of these compounds with those of their analogues incapable of association in the crystal. Unfortunately, although such structures are known—the acetates of *syn*- and *anti*-2-bromo-*p*-benzoquinone oximes and 2-chloro-*p*-benzoquinone oxime[50,51]—the low accuracy of their determination precludes a detailed analysis of the geometrical parameters of the molecules (such a comparison has been carried out for amino-derivatives of β-naphthoquinones—see below).

An oxime structure with a small contribution of the nitroso-form is also characteristic of *syn*- and *anti*-pyridine-4-carboxaldehyde oximes[52,53] and *syn*- and *anti*-pyrimidine-4-carboxaldehyde oximes[54,55]. As in the structures of *p*-benzoquinone oximes, in the crystal the molecules of these compounds form infinite chains via hydrogen bonds.

o-Quinone oximes were investigated approximately 20 years ago and the accuracy of these studies is unfortunately not very high. These compounds crystallise in two forms—orange and green. On the basis of spectroscopic and crystal-optical data, it was suggested that the more stable orange α-form corresponds to the quinone oxime structure and the green β-form corresponds to the nitrosophenol structure. The structure of the orange form was determined (on the basis of projections) for 5-methoxy-*o*-quinone 2-oxime[56]. Its molecules do indeed exist in the *anti*-configuration of the quinone oxime form and are linked into infinite chains via hydrogen bonds (Fig.16); the consideration of specific geometrical parameters would not be justified in view of the accuracy obtained. The structure of the green β-form of 5-n-propoxy-*o*-quinone 2-oxime has been determined[57] and it was found that in this case the quinone oxime form predominates (Fig.17), although the molecule has the *syn*-configuration with a strong intramolecular hydrogen bond. The nature of the absorption spectrum, which does not correspond to the oxime structure, can apparently be accounted for by the presence of this bond and a significant contribution of the nitrosophenol form.

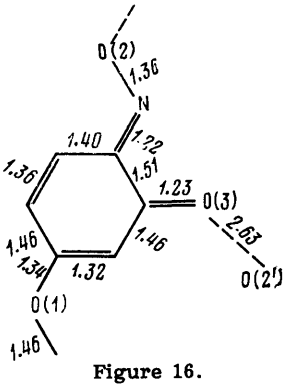


Figure 16.

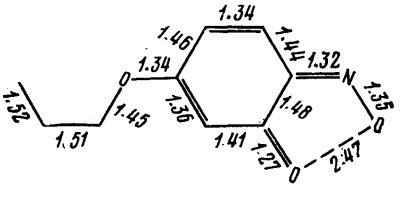


Figure 17.

The crystals of potassium *p*-nitrosophenoxide monohydrate (green)[58], magnesium *p*-nitrosophenoxide hexahydrate (reddish green)[59], and sodium *p*-nitrosophenoxide trihydrate (pale red)[60] also have different colours.

Unfortunately the accuracy of the determination of the structure of the potassium salt is insufficient for the analysis of the electronic structure of the anion. On the other hand, comparison of the geometrical parameters of the *p*-nitrosophenoxide anion in the sodium (Fig.18*a*) and magnesium (Fig.18*b*) salts showed that, as in *o*-quinone oximes, the green colour is associated with a large contribution of the nitrosophenol form, although the latter does not predominate. Comparison of these three structures also shows how much the electronic structure of the *p*-nitrosophenoxide anion depends on the nature of the cation and the system of hydrogen bonds in the crystal.

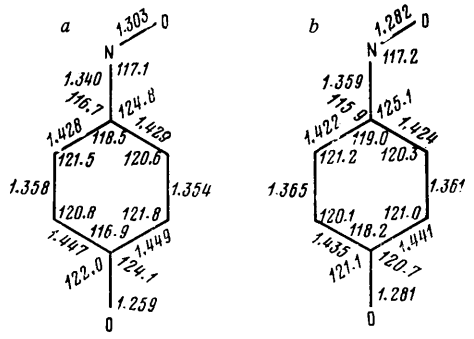


Figure 18.

In all the structures examined in this section (with the possible exception of that of triphenyl-lead 2-fluoro-4-nitrosophenoxide) the quinone oxime form predominates. The nitrosophenol structure has been found only in the molecule of 5-nitrososalicylic acid[61], where the H atom of the hydroxy-group is involved in a strong hydrogen bond with the carboxy-group, as in salicylic acid itself (Fig.19).

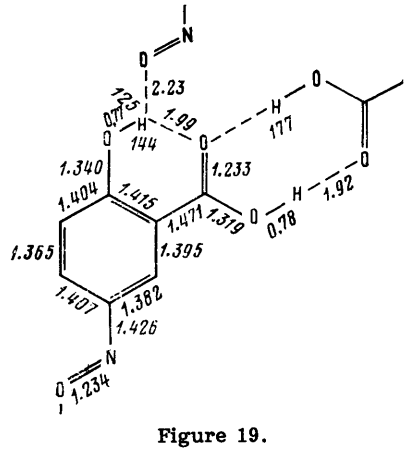


Figure 19.

1,2-Naphthoquinone 1-oxime[62] and its 6-t-butyl derivative[63] have the quinone oxime structure and the *syn*-configuration with an intramolecular hydrogen bond. On the other hand, in the metal (Ni, Cu, Hg) complexes of 1,2-naphthoquinone oximes a five-membered ring is formed in which the NO group coordinates the metal atom via the N and not the O atom, rather than a six-membered chelate ring; the ligand has the *anti*-configuration[64-67]. The copper, nickel, and zinc complexes with 1,2-naphthoquinone oxime ligands containing sulpho-groups in the 4- or 5-position have analogous structures[68-70]. The sulpho-derivatives of 1,2-naphthoquinone oximes themselves (with the sulpho-groups in the 5-, 7-, or 8-position) have the *anti*-configuration, in contrast to their analogues without sulpho-groups[71-75]; the H atom of the oxime group in these structures forms an intermolecular hydrogen bond with an O atom of the sulpho-group. The molecule of 7-hydroxyimino-8-oxoquinoline-5-sulphonic acid in the crystal[76] and its anion in the structure of the disodium salt[76] also exist in the *anti*-configuration.

It is noteworthy that in the naphthoquinone oxime molecules examined above, in both the *syn*- and *anti*-configurations, the quinone oxime tautomeric form is very pronounced: the bond lengths vary in the ranges 1.20 to 1.25 Å for C–O, 1.30–1.31 Å for C–N, 1.35–1.39 Å for N–O, and 1.47–1.52 Å for C–C (between the carbonyl and oxime groups). In the quinone oximate anion[76] the contribution of the nitroso-form is somewhat greater: the bond lengths (1.28 Å for C–O, 1.35 Å for C–N, 1.28 Å for N–O, and 1.44 Å for C–C) are close to those found in sodium *p*-nitrosophenoxide[60] (see above). The quinone oximato-ligand has similar geometrical parameters also in the metal complexes.

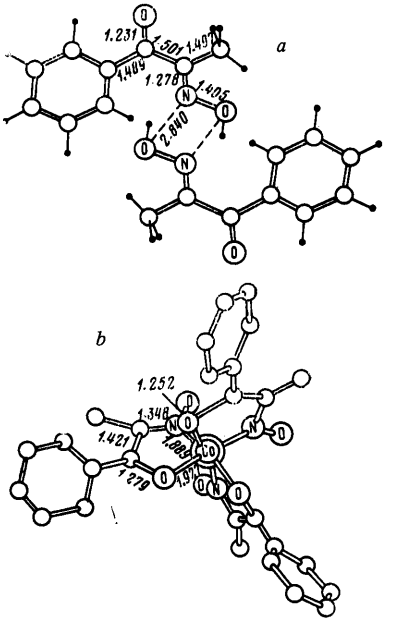
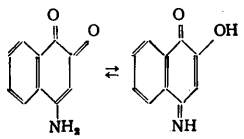


Figure 20.

The oxime form is very distinct also in the structure of 1-phenylpropane-1,2-dione 2-oxime[77] (Fig.20*a*), where the molecules are combined into centrosymmetric dimers via O–H...N hydrogen bonds, while in the cobalt complex[78] this ligand assumes an intermediate structure, like the naphthoquinone oximato-ligand (Fig.20*b*).

The example of naphthoquinone oximes shows that, although the structures with a hydrogen bond between two nucleophilic centres of potentially tautomeric systems are the main ones, they are not the only ones possible for such crystals: when the molecule contains other nucleophilic centres, for example, the sulpho-group, the *a priori* prediction of the structure requires estimates of the energies of the different variants of the resultant structure.

It must also be emphasised that the delocalisation of π-electrons, which is so characteristic of potentially tautomeric systems with hydrogen or secondary (coordinate) bonds, can be observed also in structures where such bonds are absent. The structures of 4-amino-1,2-naphthoquinones[79], where tautomerism is possible in principle, may serve as a good illustration:



The structures of 4-amino-3-bromo-1,2-naphthoquinone, its monohydrate, and methanol solvate, as well as the structures of the monohydrate of 4-amino-3-methyl-1,2-naphthoquinone, 4-diethylamino-1,2-naphthoquinone, and 4-dimethylamino-1,2-naphthoquinone have been determined[79]. In the first four structures there are intermolecular N–H...O hydrogen bonds between the NH_2 group and the CO group in the β-position. The average bond lengths in the N–C=C–C=O chain in these molecules are 1.322, 1.392, 1.405, and 1.246 Å. In the last two structures there are no hydrogen bonds, but the π-bonds are nevertheless delocalised, reflecting the significant contribution of the dipolar form $H_2\overset{+}{N}=C-C=C-\bar{O}$; however, the average bond lengths (1.358, 1.376, 1.418, and 1.237 Å) show that the delocalisation is appreciably weakened in the absence of hydrogen bonds.

V. FORMAMIDINES AND TRIAZENES

If the tautomeric rearrangement is degenerate, then X-ray diffraction makes it possible to distinguish a rapid exchange process from the symmetrical structure equalised as a result of chelate formation in those cases where the NMR method cannot provide an unambiguous answer to this question. An example of such a structure is *N*-phenylmercuri-*N*,*N'*-ditolylformamidine[80]. In the ^1H, ^{19}F, and ^{13}C NMR spectra of this and related compounds the signals of the indicator groups in the *p*-positions of the aromatic rings consist of singlets and the protons of the rings themselves give rise to a symmetrical quartet A_2B_2.

The structures of two crystallographically independent molecules, found by X-ray diffraction, are illustrated in Fig.21. The bond between the phenylmercuri-residue and the formamidine fragment is different in them: in the A molecule the Hg atom forms a normal covalent bond with the N(1) atom, having a length of 2.13(3) Å. The Hg...N(2) distance (2.68 Å) is shortened compared with the sum of the van der Waals radii by ~0.5 Å and indicates the occurrence of coordination interaction. In the B molecule the Hg'...N(2') distance (3.19 Å) is significantly greater than in the A molecule and is virtually equal to the sum of the van der Waals radii, i.e. in the B molecule the coordination interaction is either absent or very weak. At the same time, there is a weak intermolecular interaction between neighbouring type B molecules [the Hg'...N(2'') distance is 3.08 Å]. Thus the characteristics of the spectra of the *N*-phenylmercuri-derivatives of *N*,*N'*-diarylformamidines are due to the rapid reversible intramolecular exchange of the phenylmercuri-residue between the N atoms of the amidine triad. Such exchange is facilitated by the intramolecular coordination observed in the A molecule.

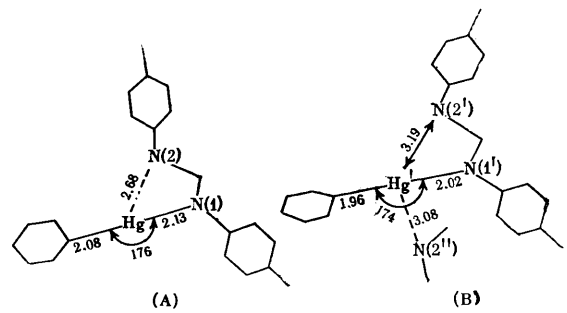


Figure 21.

In the molecule of the phenylmercuri-derivative of 2-chlorodiazoaminobenzene[81] the Hg atom forms a covalent bond with one N atom of the triazene system (Hg–N = 2.14 Å) and is coordinated to the other atom (Hg...N = 2.46 Å). The geometries of the triazene and formamidine systems are not very favourable for the formation of a secondary Hg...N bond, because the N–Hg...N angle is much smaller than the ideal value for the Hg atom (90°). Systems of this type are even more unfavourable for the formation of an intramolecular hydrogen bond.

Indeed the binding of the molecules into helical chains by N–H...N intermolecular hydrogen bonds is characteristic of the diazoaminobenzene structures. The crystals of the α- and β-modifications of diazoaminobenzene[82,83], the β-modification of *p*-bromodiazoaminobenzene[84,85], the *p*-methyl- and *p*-chlorodiazoaminobenzenes[86], and *p*,*p'*-dimethyl, *p*,*p'*-dichloro-, and *p*,*p'*-dibromodiazoaminobenzenes[87,88] are constructed in this way. Cyclic dimers are formed via N–H...N hydrogen bonds only in the α-modification of the *p*-bromodiazoaminobenzene molecule[85]. In two structures—those of *p*-nitrodiazoaminobenzene[89] and 2,4-dibromodiazoaminobenzene[90]—the N–H...N hydrogen atoms are absent. The packing of the molecules in the former structure is determined by the N–H...O hydrogen bonds with the nitro-group; a short N...Br contact has been found in the latter molecule, which may also correspond to a hydrogen bond.

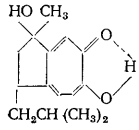
Unfortunately the accuracy of the results of all these studies is low and precludes a conclusion concerning the distribution of hydrogen atoms and bond lengths in the triazene chain.

VI. TROPOLONES

Structures with chelate rings are known for mercury (but not in its organic derivatives). Mercury tropolonate, for example, has such a structure[91]: both tropolonate ligands form chelate rings with Hg–O distances of 2.30 Å; the planes of the two ligands form an angle of 85° relative to one another. Tropolone forms symmetrical chelate complexes, similar to the mercury complex described by Allman et al.[91],

also with other metals, for example iron[92], zirconium[93], and copper[94].

Tropolone itself is a tautomeric system[95] and the independence of the signal of the hydroxyl proton in the ^{1}H NMR spectrum of concentration indicates an intramolecular process mechanism[95,96]. However, the geometry of the tropolone molecule is not optimal for the formation of a chelate ring via an intramolecular hydrogen bond and in the crystal tropolone molecules form dimers with a forked hydrogen bond incorporating both intramolecular and intermolecular components[97] (Fig.22). Dimers with a similar structure have also been discovered in the crystals of 4-isopropyltropolone[98,99], 5-isopropyltropolone[100], 3,7-dibromo-6-isopropyltropolone[100], and 5,7-dibromo-4-isopropyltropolone[101]. According to electron diffraction data[102], in the gas phase an asymmetric hydrogen bond is formed in the tropolone molecule. An intramolecular hydrogen bond is apparently also formed in 3,5,7-tribromo-6-isopropyltropolone[103] and chanootin[104]:



In the crystal of ditropolonylfuran[105] dimers having a forked hydrogen bond are formed with participation of one tropolone ring, while in the other ring only an intramolecular hydrogen bond is produced.

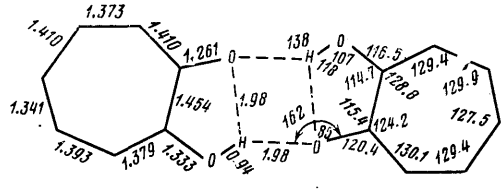


Figure 22.

Carbonotropic systems have been recently synthesised in the series of tropolone derivatives[106,107] (Fig.23). It has been shown by dynamic NMR that the activation barrier to the rearrangement A ⇌ B in solution amounts to 26 kcal mol^{-1} for the *p*-nitrophenyl ether (I). On passing to the 2,4-dinitrophenyl ether (II), it decreases to 11.7 kcal mol^{-1} and for the 2,6-dinitrophenyl ether (III) it becomes so low that, in terms of the ^{1}H NMR time scale, the molecule has an effective C_{2v} symmetry, i.e. a type (B) structure, although the electronic absorption spectra of solutions indicate an asymmetric molecular structure; the 2,4,6-trinitrophenyl derivative has a true symmetrical structure (BIV), i.e. is the first example of a zwitter-ionic Meisenheimer σ-spiro-complex. The (BIV) structure has been confirmed by X-ray diffraction[108]. The molecule in the crystal is located on a two-fold axis (Fig.24). The plane of the cyclohexadienyl ring is almost perpendicular to the remaining portion of the molecule, the angle between them amounting to 85.8°. The C(4) atom is tetrahedral, the angles at the latter varying in the range 101.9–112.4°. The bond lengths in the seven-membered ring are equalised (1.379–1.401 Å), which is characteristic of the tropylium cation. In the six-membered ring the C(3)–C(4) bond length is 1.486 Å, which is appreciably greater than the aromatic bond lengths (1.394 Å) and approaches the length of a single C(sp^2)–C(sp^3) bond (1.510 Å).[28] The lengths of the remaining C–C and C–N bonds indicate the delocalisation of the negative charge over the ring and the nitro-groups.

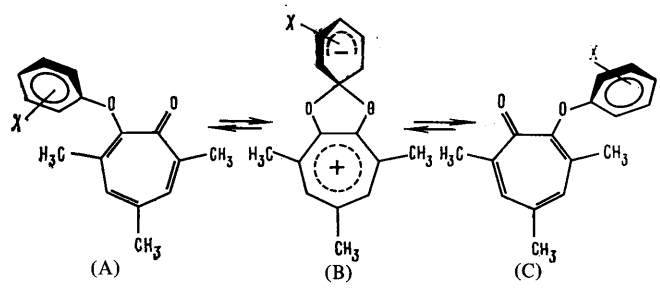


Figure 23.

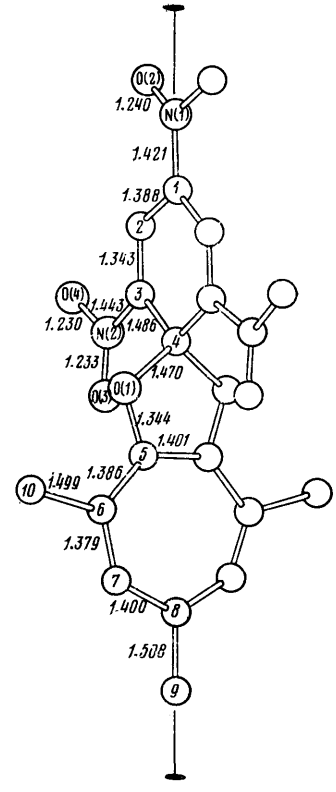


Figure 24.

X-Ray diffraction analysis of the (AIII) structure yielded particularly interesting results[108]. Despite the possibility of rotation about the O(1)–C(7) and O(1)–C(1) bonds (Fig.25), the molecule assumes a conformation in which the C(1) atom approaches to the maximum possible extent

the O(2) atom and the C(1)...O(2) distance, which is 2.451 Å, is significantly shorter than the sum of the van der Waals radii (~3.2 Å).[21] As in the (BIV) structure, the plane of the six-membered ring is almost perpendicular to that of the tropolone system (the angle between them is 84.9°), i.e. the conformation of the (AIII) molecule is optimal for the closure of a five-membered ring with formation of a spiro-structure of type (BIV). Furthermore, the C(1) atom is displaced by 0.09 Å from the plane of the three atoms linked to it, in the direction of the O(2) atom, while the C(1)...O(2) line is approximately perpendicular to the O(1)C(1)C(2)C(3) fragment. All these geometrical features show that a configuration fairly close to the structure of the transition state in the first stage (A ⇌ B) of the intramolecular rearrangement A ⇌ C obtains in the (AIII) structure. These geometrical features actually explain the exceptionally high frequency of the migration of the 2,6-dinitrophenyl group in (AIII) solutions.

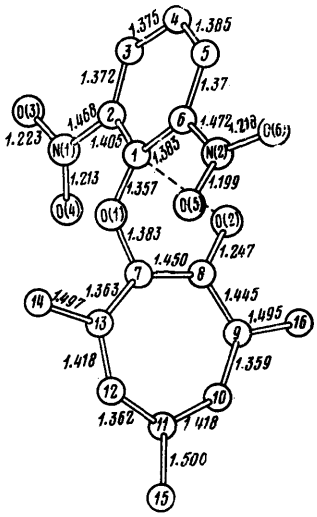
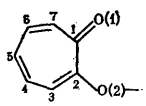


Figure 25.

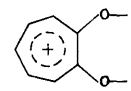
The observed molecular conformation is possible only in the presence of a strong C(1)...O(2) interaction. In the absence of such interaction, the molecule assumes a transoid configuration relative to the C–O bond, as, for example, in *p*-chlorobenzoyltropolone[109]. It is noteworthy that the energy barriers to the *O,O'*-aroyl migrations in tropolone derivatives are much higher than the barriers to the migrations of the 2,6-dinitrophenyl group[106] and there is thus a direct relation between the structure of the molecule and its dynamic behaviour. At the same time it must be emphasised that the occurrence of an intermediate state with a strong intramolecular C(1)...O(2) interaction in the (AIII) crystal proved to be possible as a result of a particularly favourable geometry of this system[107].

Comparison of data for tropolone derivatives makes it possible to distinguish three limiting types of their electronic structure. Type I is a structure with localised double bonds:



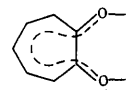
The structure of *p*-chlorobenzoyltropolone[109] with the bond lengths C=O = 1.225, C–O = 1.388, and C(1)–C(2) = 1.459 Å, while the average values of the remaining bonds are C–C = 1.419 Å and C=C = 1.338 Å, is closest to this type.

Type II is the structure of the tropylium cation (a six-electron π-system) with delocalisation of the π-electrons over the ring:



A type II structure obtains in tropolone hydrochloride[110] (with the bond lengths C–O = 1.365 and C–C = 1.38–1.41 Å) and the 2,4,6-trinitrophenyl ether of tropolone[108] (C–O = 1.344 Å and C–C = 1.379–1.401 Å).

Finally type III is a structure with a delocalised π-electron system not including the C(1)–C(2) bond but including the C–O bond (a ten-electron π-system):



Sodium tropolonate[111,112] (C–O = 1.278 Å, C(1)–C(2) = 1.478 and with the remaining C–C bond lengths of 1.388–1.426 Å) and the metal complexes mentioned above have this structure. This form makes some contribution to the structures of numerous hydrogen-bonded tropolone derivatives, which is manifested primarily by a lengthening of the C=O bond (~1.25–1.26 Å) and a shortening of the C–O bond (~1.33–1.35 Å); the C(1)–C(2) bond length is 1.45–1.50 Å, the remaining C–C bond lengths in the ring are 1.40–1.44 Å, and the C=C bond lengths are 1.35 to 1.37 Å.

The considerable delocalisation of the π-electrons in these systems, as in the systems discussed previously, is due precisely to the formation of a hydrogen bond. SCF–MO calculation[113] without allowance for this bond leads to a more delocalised system [C=O = 1.258 Å, C–O = 1.389 Å, C–C = 1.452–1.462 Å, and C=C = 1.355–1.357 Å; the C(1)–C(2) bond length does not differ from that of the other C–C bonds in the ring].

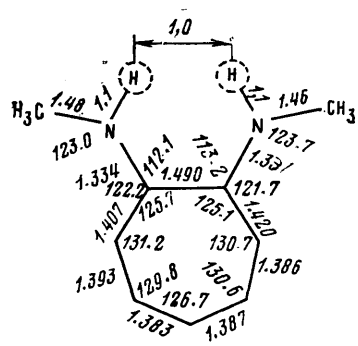


Figure 26.

In contrast to these derivatives, the nitrogen analogue of tropolone—1-methylamino-7-methyliminocyclohepta-1,3,5-triene—has a type III structure in an almost pure form[114]. According to X-ray diffraction data (Fig.26), a hydrogen

atom in the molecule is distributed between two equivalent positions at a distance of ~1.0 Å from one another and at a distance of ~1.1 Å from the nearest N atom. A detailed analysis of thermal vibrations showed that this structure is not a result of a disordered statistical superposition of two "tautomers" but corresponds to a symmetrical system with a very low energy barrier to the transition of the H atom from one potential well to another. This description is consistent with infrared spectra[115] and with ^{1}H NMR spectra[114], in which the protons of the CH_3 groups give rise to a singlet signal even at −80 °C.

VII. β-DIKETONES

β-Diketones also form symmetrical chelate rings with the bond lengths C−C ≅ 1.39 Å and C−O ≅ 1.27 Å in complexes with most metals (see, for example, Lingafelter and Braun[8]). The acetylacetonate anion in the potassium salt also has a structure with delocalised bonds[116]. However, β-diketones can also give rise to a C-form with an Hg atom, which has not been found for tropolonate complexes.

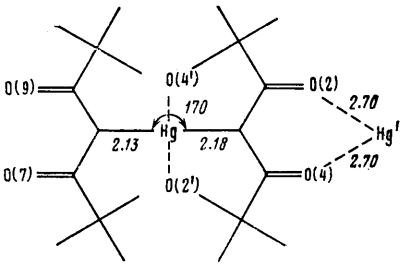
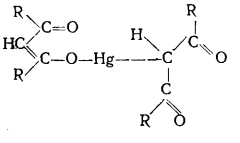


Figure 27.

Mercury bispivaloylmethanate has such a structure in the crystalline state[117,118] (Fig. 27). The Hg atom in this molecule forms somewhat lengthened Hg−C bonds (2.13 and 2.18 Å) with the two dipivaloylmethanate groups (the normal Hg−C bond length is 2.07−2.11 Å) and weak coordinate bonds having a length of 2.70 Å with the two oxygen atoms of a neighbouring dipivaloylmethanate group (the length of the covalent Hg−O bond is 2.03−2.07 Å. The ^{1}H NMR spectra showed that in solution in chloroform the molecules of this compound are monomeric, but a weak signal at 5.75 p.p.m. indicates the presence of ~5% of the enolic form together with the initial diketo-form. According to Fish[119], the content of the enolic form in solution in ethanol rises to 50% and the molecular structure is described by the formula



The molecules of (nonane-4,6-dionyl)trimethylplatinum are dimeric both in the crystal and in solution[118]. In this dimer (Fig. 28) the Pt−O bonds (2.14 and 2.16 Å) (the normal value is 1.97 Å) may be regarded as the main ones, while the Pt−C bond (2.39 Å) is "additional" (the normal length of the Pt−C σ-bond is 2.02 Å), i.e. the bonds are more equalised in this structure.

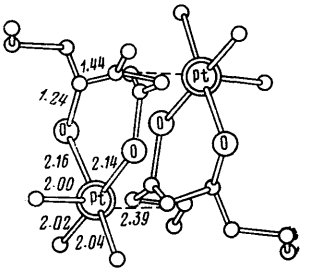


Figure 28.

According to X-ray diffraction studies, the non-coordinated β-diketone molecules exist in the enolic form and have a cisoid conformation with a very strong intramolecular hydrogen bond. Depending on the nature of the substituents, both an almost symmetrical structure with approximately equalised bonds, for example, in benzoylacetone according to X-ray diffraction data[120] and neutron diffraction data[121], and a highly asymmetric structure with a distinct predominance of one of two enolic forms, for example, in 1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dione[122] (Figs. 29*a* and 29*b*), can obtain.

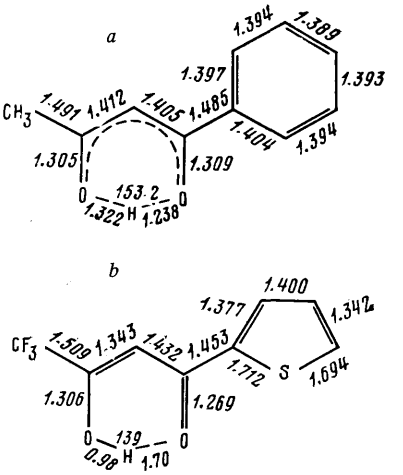


Figure 29.

The structure of the last compound agrees with the results of a calculation by the CNDO/2 method[123], which showed that the proton should be localised at the carbonyl group with the more electronegative β-substituent. However, a fully equalised structure with a highly symmetrical hydrogen bond has not been found among β-diketones. In all the structures

where the position of the hydrogen atom has been determined fairly reliably from X-ray or neutron diffraction data (see, for example, Refs.124–129), the atom is displaced towards one of the oxygen atoms and this displacement is correlated with the difference between the C–C and C–O bond lengths. It is noteworthy that there is no fundamental difference between symmetrical and slightly asymmetric hydrogen bonds[130]. The adiabatic potential of a hydrogen atom involved in very strong hydrogen bonds has a broad and shallow minimum and even the very weak perturbations due to the asymmetry of the environment of the molecule in the crystal are sufficient to infringe the symmetry of this bond[131].

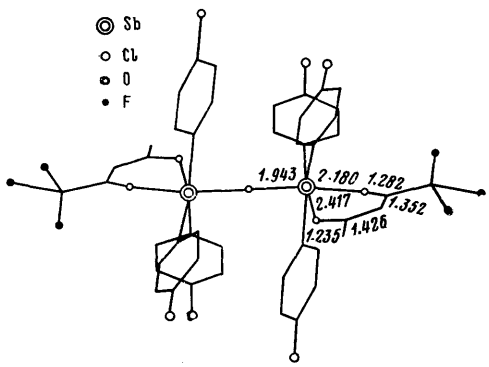


Figure 30.

A strong intramolecular O–H...S bond is formed in 3-mercapto-1,3-diphenylprop-2-en-1-ol [132] (according to neutron diffraction data, the bond lengths are O–H = 1.024 Å, H...S = 1.904 Å, and O...S = 2.865 Å), i.e. the compound exists in the crystal in the enolic (and not the thioenolic) form; the C–O bond (1.321 Å) is comparatively long, while the length of the C–S bond (1.675 Å) is close to that of a double bond. The chelate ring in μ-oxobis[tris(*p*-chlorophenyl)(1,1,1-trifluoropentane-2,4-dionato)antimony] has a highly asymmetric structure[133] (Fig.30), while in the octahedral acetylacetonate complexes [(acac)CH_3SbCl_3], [(acac)$(CH_3)_2SbBr_2$], and [(acac)Ph_2SbCl_2] [134] the chelate rings are symmetrical. In (1,3-diphenylpropene-1,3-dionato)triphenyltin[135], with a trigonal-bipyramidal coordination of the metal atom, the equatorial Sn–O(1) bond (2.094 Å) is shorter than the axial Sn–O(2) bond (2.276 Å). Accordingly the bonds in the diketonate ligand are also non-equivalent: the lengths of the bonds closest to O(1) are C–O = 1.29 Å and C–C = 1.36 Å, while those of the bonds closest to O(2) are C–O = 1.26 Å and C–C = 1.40 Å.

Phosphonia-β-diketones have a somewhat different structure. The α-triphenylphosphoniabenzoylacetone cations also exist in the enolic form in the crystal but have the *trans*-configuration, forming a hydrogen bond with Cl^- (Fig.31) or BF_4^- ions[136,137]. The chloride of α-triphenylphosphoniaacetoacetic ester has a similar structure[138]. In contrast to the *cis*-enols, in the *trans*-enols the planarity of the enolic system is appreciably infringed and the bond lengths are closer to the standard values: C–C = 1.49–1.56 Å, C=C = 1.31–1.37 Å, C–O = 1.32–1.33 Å, and C=O = 1.17–1.24 Å.

Acetylacetone has been investigated by electron diffraction in the gas phase and it has been observed that at the experimental temperature (~105 °C) the content of the enolic form in the gas is 66%.[139] The geometrical parameters of the enolic and diketo-forms are presented in Fig.32. At room temperature the equilibrium is displaced towards the symmetrical enolic form according to electron diffraction data[140]. The electron diffraction data for trifluoroacetylacetone[140] and hexafluoroacetylacetone[141] also agree best with the symmetrical enolic structure.

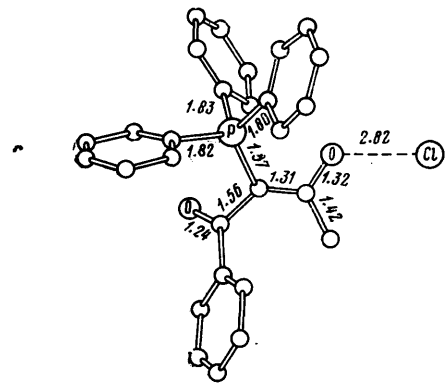


Figure 31.

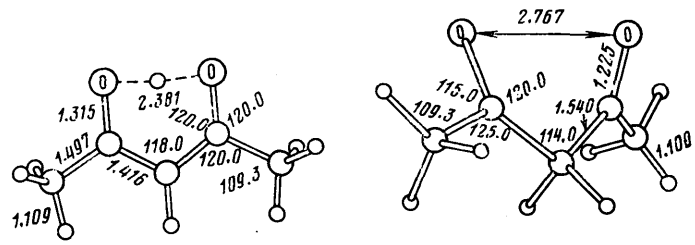


Figure 32.

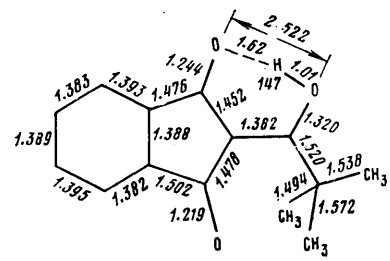


Figure 33.

In the 2-pivaloylindan-1,3-dione molecule[142] one of the carbonyl groups is involved in a keto–enol system with a strong intramolecular hydrogen bond, while the other remains free (Fig.33). This structure makes it possible to observe particularly distinctly the lengthening of the C=O bond in the chelate ring and the shortening of the C–C bond in

the latter, in conformity with the partial contribution of the second tautomeric form to the structure.

In the series of acetylacetone derivatives, as in the tropolone series, carbonotropic tautomerism has also been observed[107], but there are virtually no X-ray diffraction data for compounds of this class. X-Ray diffraction analysis of the picryl derivative of acetylacetone *N,N'*-dimethyldiimine[143], on the basis of which the intramolecular migration of the picryl group between the two N atoms might have been postulated (Fig.34), showed that this compound is a *C*-derivative (formula C).

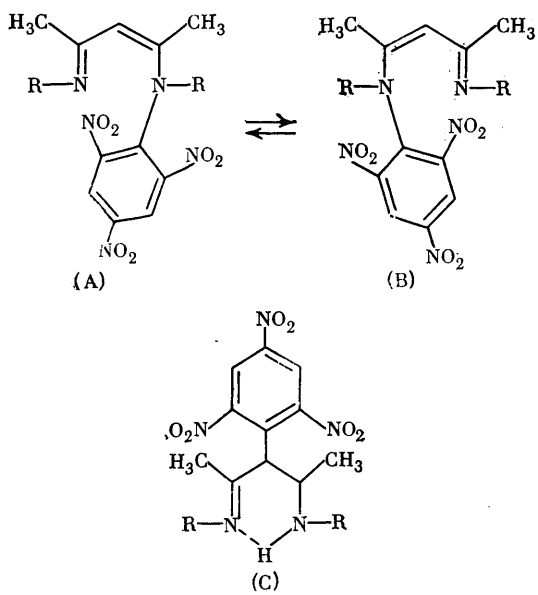


Figure 34.

VIII. MOLECULAR GEOMETRY AND INTRAMOLECULAR REARRANGEMENTS

Thus the formation of hydrogen (in the case of prototropism) or secondary (in the case of metallo- and carbono-tropism) bonds is characteristic of all tautomeric and potentially tautomeric systems. The relation between the geometries of the molecules and their capacity for intramolecular rearrangements has been traced for some of the examples described above.

The relation between the geometry of the molecule and its ability to undergo the *trans*-acylation reaction has been noted in X-ray diffraction studies on naphthazarine[144] (Fig.35) and tetramethylnaphthazarine[145] diacetates. In these molecules the planes of the acetyl groups are almost perpendicular to the plane of the naphthazarine ring, but are nevertheless somewhat inclined towards the quinonoid oxygen atom, which shortens the C...O distances to 2.68–2.75 Å, although, at least for the first molecule, there is a possibility of the deviation of this group in the opposite direction. Thus even in the ground states of these molecules there exists a basis for the transfer of the acyl group to the neighbouring O atom. However the C...O interaction in these systems is weak and does not distort the C=O and C–O bond lengths.

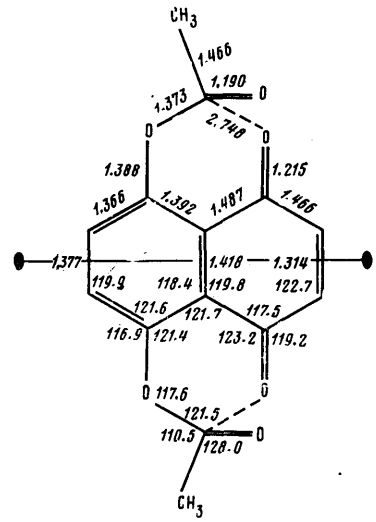
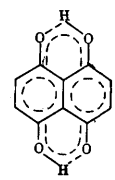
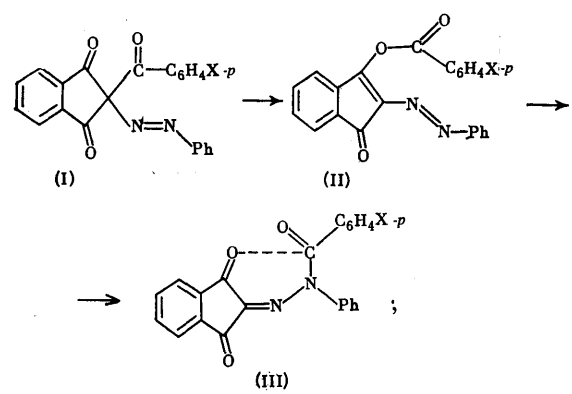


Figure 35.



In naphthazarine itself there is a strong slightly asymmetric O–H...O hydrogen bond, so that the structure is nearly mesomeric, but with a slight predominant contribution of the 4,8-dihydroxy-1,5-naphthoquinone form[146]. Shortened intramolecular C...O distances between the carbon atom of the benzoyl group and the oxygen atom of the carbonyl group (2.673, 2.638, and 2.835 Å) have also been found in the structures of the 2-(*N*-benzoyl-*N*-phenylhydrazones) of indan-1,2,3-trione (III),[147,148] which are formed instead of the expected enol benzoates (II) on thermal rearrangement of the corresponding azo-compounds (I):



X = H (*a*), Br (*b*), or t-Bu (*c*).

In the crystal these molecules can exist both in the *syn*-configuration [compound (IIIa) and one of the independent molecules of compound (IIIb)] and in the *anti*-configuration [the second independent molecule of compound (IIIb) (?) and compound (IIIc)], the unusual stability of the sterically

strained *syn*-form being probably caused by the C...O interaction mentioned above. This interaction creates almost ideal conditions for the rearrangement (III) ⇌ (II), which apparently makes the (II) → (III) transition very rapid during the reaction and precludes the observation of the intermediate formation of (II). One should note that the C...O interaction observed in these structures is fairly weak and does not alter appreciably the bond lengths in the *syn*-form compared with the *anti*-form.

IX. FULVENES

The derivatives of pentafulvenes are also interesting keto-enol systems. 6-Hydroxyfulvene-1-carboxaldehyde has been investigated by X-ray and neutron diffraction[149]; two of its nitro-derivatives—2,3-diacetyl- and 2,3-dibenzoyl-5-nitrocyclopentadiene—have also been subjected to X-ray diffraction analysis[150]. The diketo-form (I) (Fig.36), a tautomeric equilibrium between the enolic fulvene forms (II) (which appears most probable on the basis of spectroscopic data), or a delocalised symmetrical structure (IV) are possible in principle for these compounds. The ^{1}H NMR data for the nitro-derivative also do not conflict with structure (III). Studies[149,150] have shown that in the crystals of all three compounds structure (IV) is formed.

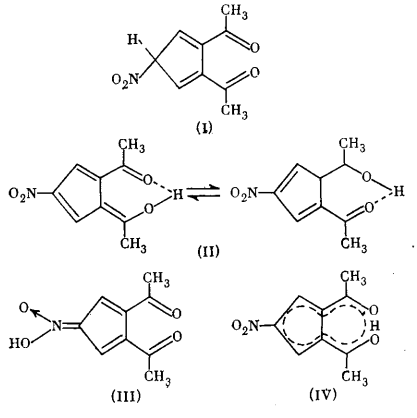


Figure 36.

The enolic hydrogen atom is located at approximately equal distances from both oxygen atoms (although in an X-ray diffraction study of 6-hydroxyfulvene-1-carboxaldehyde the hydrogen atom gave rise to a double electron density peak, but in the remaining cases the location of this atom was unambiguous) and the molecular symmetry is close to C_{2v}. The length of the central C–C bond is 1.462–1.467 Å, which is close to that of a single bond in cyclo-octatetraene (1.462 Å), while the lengths of the remaining C–C and C–O bonds are close to values correspondng to a bond order of 1.5, i.e. the delocalisation involves mainly the outer ring and affects the central bond to only a slight extent. Quantum-chemical calculations have led to an analogous conclusion[150].

In the crystal of the nitrogen analogue—*N*,*N*′-diphenyl-6-aminopentafulvene-2-aldimine[151]—the hydrogen atom is distributed between two positions (Fig.37), which can be a result of either a statistical superposition of two asymmetric forms, which can undergo tautomeric transitions only in solution, or of the migration of the hydrogen atom between two equilibrium positions also in the crystal. Analysis of thermal vibrations suggests that preference should be given to the last variant.

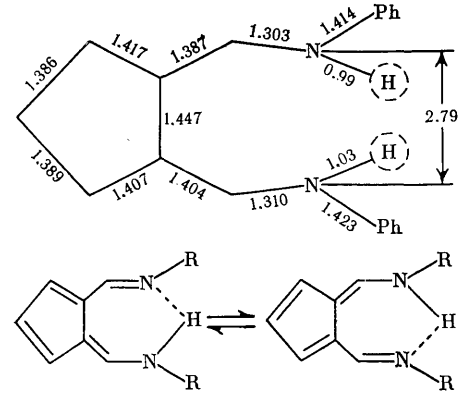


Figure 37.

* *
*

Thus the data examined have shown that in all cases of potentially tautomeric systems without exception a coordination interaction has been observed (a hydrogen bond in prototropic systems), resulting in a greater or smaller contribution of both possible tautomeric forms to the structure and ultimately in a resonance hybrid with equal contributions of both forms. The occurrence of hybrid forms in the crystal implies that their formation in the tautomeric transition requires a minimal energy expenditure. One can therefore assume that in systems where there is a possibility of intramolecular coordination, the tautomeric transformation in solution also proceeds via the formation of hybrid forms with this type of coordination.

One can also assume that in systems with highly asymmetric secondary (hydrogen) bonds, the tautomeric transition takes place more readily the stronger this bond. On the other hand, if a structure close to a resonance hybrid of two tautomeric forms obtains in the crystal, it is most likely to be stable also in solution, i.e. the system is not tautomeric. The latter is valid, for example, for the Meisenheimer tropolone spiro-complex discussed in this review. In order to confirm the general nature of the relations indicated and to obtain quantitative estimates, joint systematic studies on the geometry and tautomeric behaviour of the molecules, which are virtually completely lacking at the present time (particularly for metallotropic compounds), are necessary.

For systems with intermolecular coordination, the appearance of a hybrid transition state requires the formation of associated species, apparently with a cyclic structure, and kinetic studies are necessary for the solution of the problem of the mechanism of the transition. There is as yet no direct confirmation of the mechanism of tautomeric transitions via associated molecular species but the characteristics of certain exchange reactions (the inverse dependence of the reaction rate on temperature, overall reaction order of ~4) can be accounted for precisely by the formation of associated

species. The exchange reaction between trimethyltin phenoxide and thiophenoxide can serve as an example[152].

The solution of this and many other problems of tautomeric transformations requires further joint structural and kinetic investigations.

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