Tetrahedron, 1962, Vol 17, pp 239 to 241 Pergamon Press Ltd Printed in Northern Ireland

CONJUGATION IN SYSTEMS WITH A TETRAHEDRAL ATOM—DIARYLPHOSPHINIC ACIDS

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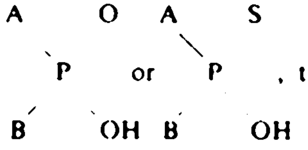
(*Received* 3 *April* 1961)

Of the two methods for the transmission of the mutual influence of atoms—by chain induction and by conjugation—only the latter is determined by steric factors. π-Bonds must be coplanar. The influence of an unsaturated substituent coupled to the reaction centre by a system of conjugated bonds sharply diminishes when it is removed from the plane of the system, for example, through steric hindrance, which is shown in the physical properties of the substances and in the velocity and equilibrium constants of their chemical reactions. This phenomenon has acquired the name of the secondary steric effect.

On $\delta\rho$ analysis, the secondary steric effect leads to a deviation from the linear relationship $\log \frac{k}{k_0} = \rho\delta$, which is connected with a change in the value of δ on disturbing the conjugation of the substituent with the transmitting chain and the reaction centre.[1]

It was found earlier that, on $\delta\rho$ analysis of the influence of a substituent on the strength of acids of phosphorus of the general type  $(A)(B)P(=O)OH$ or $(A)(B)P(=S)OH$, the linear relationship $pk = pk_0 - \rho\Sigma\delta$ in various media was well maintained for oxyacids and thioacids of phosphorus with the most diverse substituents A and B,[2-6] except for the case in which both substituents A and B are phenyl or *p*-tolyl groups.[3] It was shown, in fact, that δ for a phenyl group has a constant value of $-0{\cdot}481$ with any second substituent on the phosphorus atom: hydroxyl, alkyl or substituted alkyl, alkoxyl, aroxyl, etc, but changes to $-0{\cdot}592$ in the case where the second substituent on the phosphorus is also a phenyl group.

For the *p*-tolyl group, the value of δ, $-0{\cdot}602$ with any of the substituents enumerated above, changes to $-0{\cdot}723$ when two tolyl groups are present in the molecule.

To explain this phenomenon it was postulated that this change in the value of δ for phenyl and *p*-tolyl when two such groups are present in the molecule is connected

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[1] R. U. Taft. Paper in the symposium *N'yamena Prostranstvennyye effekty v organicheskoi khimi* [Steric Effects in Organic Chemistry] pp. 581–584. Foreign Literature Publishing House, Moscow (1960).

[2] M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* **110**, 393 (1956).

[3] T. A. Mastryukova, T. A. Melent'yeva, A. E. Shipov and M. I. Kabachnik, *Zh. Obshch. Khim.* **29**, 2178 (1959).

[4] M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov and T. A. Melent'yeva, *Dokl. Akad. Nauk SSSR* **124**, 1061 (1959).

[5] M. I. Kabachnik, T. A. Mastyukova, A. F. Shipov and T. A. Melent'yeva, *Tetrahedron* **9**, 10 (1960).

[6] M. I. Kabachnik, S. T. Ioffe and T. A. Mastryukova, *Zh. Obshch. Khim.* **30**, 2763 (1960).

with a steric disturbance of the conjugation of the π-electrons of the system of aromatic rings with the P=O bond.

The idea of the steric disturbance of conjugation in the case under consideration needs to be specified somewhat more precisely.

The usual phenomena of this type are associated with the steric hindrance of coplanarity. This is the case in the disturbance of conjugation in purely carbon π-bond systems, in which, as is well known, conjugation ensures the planarity of the arrangement of substituents about the sp^2 hybridized carbon atom (Fig. 1). In the case of the diarylphosphonic acids, the central multiple-bonded phosphorus atom retains its tetrahedral configuration (sp^3 hybridization; one unhybridized d-electron takes part in the π-bond). Hence, of the two phenyl rings bound to the phosphorus atom, only one can be coplanar with the plane of symmetry of the electron cloud of the P=O π-bond. The second ring lies in another plane intersecting the plane of the conjugated system along the axis of the P=O bond (Fig. 2). According to a second alternative, both phenyl rings are non-coplanar with the plane of symmetry of the P=O π-bond, the planes of the rings intersecting it at equal or unequal angles.

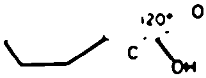

FIG. 1. sp^2 hybridization and conjugation; benzoic acid; the atoms of the benzene ring and the CO_2 group lie in the same plane.

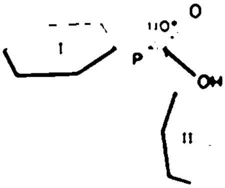

FIG. 2. sp^3 hybridization and conjugation; diphenylphosphinic acid; the atoms of benzene ring (I) and the P=O group lie in the same plane; the atoms of benzene ring (II) and the P=O group lie in a different plane intersecting the first along the axis of the P=O bond.

In monophenylphosphinic acid and its hydrogen esters (Fig. 3), the plane of symmetry of the P=O π-bond can always be orientated in coplanarity with the plane of the benzene ring. When the conjugation is disturbed, the value of δ for the phenyl ring must diminish, approaching the value of δ for alkyl groups. In diphenylphosphinic acid, one of the phenyl rings (or both) is present under conditions less favourable for conjugation than in the monophenyl derivative; this must lead to a diminution in the value of δ to some value characterizing the mean degree of disturbance of the conjugation. Experiment shows that this change amounts to approximately 20 per cent of the basic magnitude of δ.

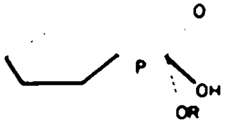

FIG. 3. Phenylphosphinic acid and its hydrogen esters; the atoms of the benzene ring and the P=O group lie in the same plane, the OH and OR groups are at the apices of a tetrahedron.

The fact that this change is not connected with the steric hindrance of coplanarity is shown by the absence of the effect with a branched alkyl radical (isopropyl or cyclopentyl) in place of the second aromatic group; in these cases no deviation from the linear relationship $pk - pk_0 - \rho\Sigma\delta$ is observed when the usual value of δ for a phenyl group is employed (−0·481). It follows from this that the disturbance of the conjugation is a phenomenon specific to the simultaneous presence of two aromatic (or possibly, in the general case, unsaturated) substituents on the phosphorus.

It is of interest to note that when two different aromatic substituents are introduced (for example, phenyl and *p*-tolyl), good agreement with Hammett's equation is obtained with the use of the values of δ deduced from the symmetrical acids (that is, 0·592 for the phenyl group and 0·723 for the tolyl group).

Thus, when a second aromatic grouping is attached to the phosphorus atom, a regular change in the value of the constant δ, connected with a disturbance of the conjugation, is observed.

The phenomenon considered must be extremely general for π-conjugated aromatic or unsaturated systems including an atom with a tetrahedral (or other non-planar) distribution of bonds.