LITERATURE CITED

1. L. S. Éfros, B. A. Porai-Koshits, and S. G. Farbenshtein, Zh. Obshch. Khim., 23, 1961 (1953).
2. H. Balli and R. Maul, Helv. Chim. Acta, 59, 148 (1976).
3. A. M. Simonov and A. N. Lomakin, Zh. Obshch. Khim., 32, 2228 (1962).
4. C. Blaise, A. Bouanane, and P. Lochon, Bull. Soc. Chim. Fr., Nos. 11-12, 1843 (1976).
5. G. A. Mokrushina and N. P. Bednyagina, Khim. Geterotsikl. Soedin., No. 10, 1397 (1970).
6. A. W. Hofmann, Chem. Ber., 20, 1791 (1887).
7. J. Meyer, J. Prakt. Chem., 92, 255 (1915).

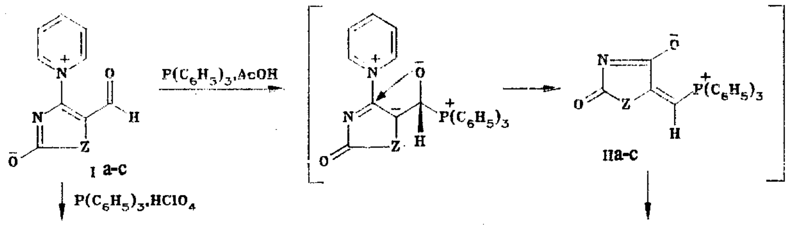
RELATIONSHIP BETWEEN THE CONSTANTS OF GEMINAL SPIN-SPIN COUPLING OF PHOSPHORUS AND HYDROGEN ATOMS AND THE CHANGES IN THE CHROMOPHORE LINK IN AZOLO[4,5-d]OXAPHOSPHOLENES AND THEIR PROTONATION PRODUCTS

S. S. Lukanyuk and R. O. Kochkanyan

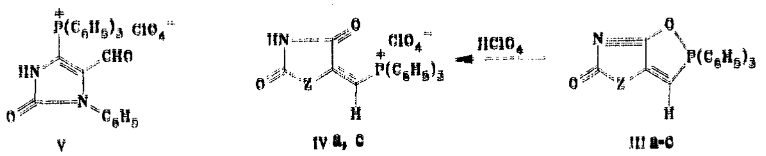
UDC 543.422.25:547.783'341

Data on the linear dependence of the constants of geminal spin-spin coupling of the phosphorus and hydrogen atoms on the long-wave absorption maxima in the electronic spectra for azolo[4,5-d]oxaphospholenes and their acyclic isomeric salts were obtained. The effect of the substituents and conformational factors on the indicated dependence was studied.

The spin-spin coupling constants (SSCC) of the phosphorus and hydrogen nuclei constitute an important characteristic in the determination of the structures of organophosphorus compounds. The tendency for the SSCC to change is not always fixed as a function of the number of bonds between the nuclei and is due to their electronic environment and structural factors. According to [1], in triethyl phosphate the SSCC decrease as the distance from the hydrogen atoms increases, so that $J_{CH_2-P} = 8.38$ Hz and $J_{CH_3-P} = 0.76$ Hz, whereas in compounds with an alkyl group bonded directly to the phosphorus atom the SSCC are greater for the β protons than for the α protons ($J_{H_\alpha-P} = 14.2$ Hz; $J_{H_\beta-P} = 30.0$ Hz) [2]. In connection with the synthesis of new two-ring systems of the types oxaphospholeno[4,5-d]azolinones (III) and acyclic trans-E (IV) and cis-Z (VII) conformers of 1-aryl-5-triphenylphoniamethylidene-imidazolidine-2,4-dione, uracil betaines VIII, and azoles V with phosphonium cations it seemed possible to follow the effect of changes in the chromophore link that bears the terminal coupling nuclei on the SSCC (J_{HP}). As we have previously reported [3], the reactions of betaines I with triphenylphosphine proceed, depending on the character of the acid used, either as a result of attack on the carbon atom of the formyl group with subsequent sigmatropic rearrangement of the oxygen atom in the 4 position of the azole ring or as a result of direct exchange of the pyridinium cation for a phosphonium group.

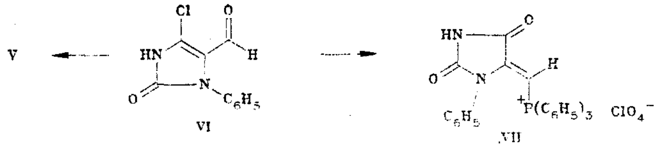


Institute of Physical Organic Chemistry and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340048. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1051-1055, August, 1985. Original article submitted May 23, 1984; revision submitted November 5, 1984.

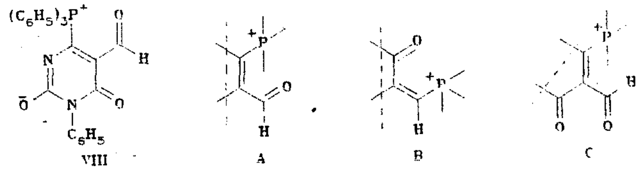


I—IV a Z=N—C$_6$H$_5$, b Z=S, c Z=N(p-Br—C$_6$H$_4$)

In the first case new two ring systems of oxaphospholeno[4, 5-d]azolinone (III) type are formed in acetic acid, whereas in the second case phosphonium salts V are formed in the presence of perchloric acid. Oxaphospholeno[4, 5-d]imidazolinone IIIa has a relatively high basicity (pK_{BH^+} = 5.43) and is protonated at the nitrogen atom in the 3 position of the heteroring with cleavage of the phosphorus—oxygen bond to acyclic salt IVa (the trans-E isomer). Like betaine perchlorate Ia, 1-phenyl-4-chloro-5-formylimidazolinone (VI) reacts with triphenylphosphine in acetic acid to give V, whereas the cis-Z isomer of 1-phenyl-5-triphenylphosphoniamethylideneimidazolidine-2,4-dione perchlorate (VII) was isolated from the reaction mixture in aprotic media.



The electronic spectra of the azole betaines that contain triphenylphosphonium (Va) and pyridinium (Ia) cations, as well as the spectrum of the previously obtained uracil betaine VIII [4], differs from the spectrum of oxaphospholeno[4, 5-d]azolinone Ia and acyclic salts Iva and VII with respect to the presence of a charge-transfer band (CTB) due to the intramolecular donor-acceptor interaction. This band undergoes a bathochromic shift on passing from VIII (λ_{max} = 358 nm) to V (λ_{max} = 377 nm) and vanishes upon acidification of solutions of these compounds. A new chromophore (the band at 331 nm) associated with π—π^* transitions in the β-phosphoniavinylformyl fragment, which is structurally similar to the chromophore in trans-E conformer IV (B), develops in the case of V.



Two absorption bands with λ_{max} 274 and 297 nm, which are due to splitting of the chromophore, as represented in fragment C, appear when uracil betaine VIII is protonated. In general form, the electronic spectra for both cyclic oxaphospholeno[4, 5-d]-azolinones Ia-c and their acyclic salts IVa, c and VII are virtually monotypic and consist of three principal bands with λ_{max} 270, 277, and 311-329 nm (the α, β, and γ bands, respectively). The latter band undergoes a certain degree of hypsochromic shift upon protonation. The long-wave maximum in the spectrum of the cis-Z isomer of 1-phenyl-5-triphenylphosphoniamethylideneimidazolidine-2,4-dione perchlorate (VII) is shifted hypsochromically as compared with the trans-E form (IVa). As we have previously noted [3], the PMR spectra of these isomers also differ. In contrast to the trans-E form, in the cis-Z form the protons of the phenyl ring in the 1 position of the imidazole ring and the two phenyl groups attached to the phosphonium group form an aromatic cluster in which the four protons of the phenyl group bonded to the imidazole ring lie in the zone of two aromatic rings of the phosphorus atom. This leads to shielding of these protons and to a shift of their signal to stronger field. The conformational analysis and determination of the chemical shifts of the protons from the calculated Johnson and Bovey parameters [5] are in agreement with the experimentally observed values.

A satisfactory correlation of the J_{HP} constants with the γ bands responsible for the π—π^* transitions in the chromophore link was observed for two-ring oxaphospholeno[4, 5-d]

TABLE 1. Spectral Parameters of IIIa-c, IVa-c, and VII

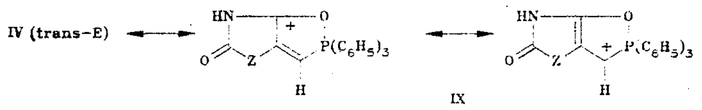
Compound	J_{H-P}	γ-Band, λ_{max}, nm (log ε)	E, eV
IIIa	17	329 (3,9)	3,76
IIIb	19	327 (3,7)	3,79
IIIc	18	327 (3,9)	3,79
VII	10	315 (4,1)	3,93
IVa	10	316 (4,0)	3,92
IVc	6	311 (4,0)	3,98

azolinones IIIa-c and their isomeric salts IVa, c and VII. The equation, calculated by the method of least squares, that links the λ_{max} and J_{HP} values has the form

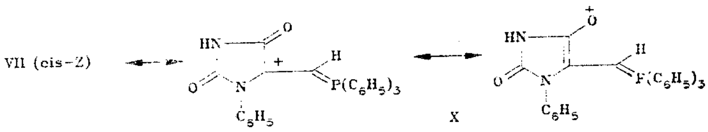
$$\lambda_{max} = (302 \pm 2) + (1.4 \pm 0.2) J,$$

for which R (the correlation coefficient) = 0.98, and S_0 (the overall dispersion) = 10.4%. The physical significance of the correlation can be explained if one takes into account the change in the electron densities on the coupling nuclei, which affects both the SSCC and the locations of the long-wave maxima (see Table 1). According to the data of Pople and Santry [6], polarization of the electron cloud by the nuclear spins (the Fermi-contact contribution) and the dipole orbital interactions make a substantial contribution to the geminal SSCC; the higher the energies of the indicated components, the smaller their contribution to the SSCC. This is in agreement with the dependence that we observed, in which a hyposochromic shift of the long-wave maximum, which corresponds to an increase in the energies of the π–π* transitions, leads to a decrease in J_{HP}.

The J_{HP} value decreases on passing from 2,2,2,4-tetraphenyl-1,2-Δ^3-oxaphospholeno[4,5-d]imidazolin-5-one (IIIa) (pK_{BH^+} = 5.43) to its acyclic salts IVa and VII, in which protonation induces a positive charge on the phosphorus atom and, upon the whole, decreases the basicity of the compound. A similar pattern was also previously observed [7] in a series of ethylene derivatives in which one of the hydrogen atoms was replaced by various electron-acceptor groups. The J^{gem}_{HH} constants are related by a linear inversely proportional dependence to the electronegativities of the substituents. In the opinion of the authors, electronegative substituents decrease the electron density around the protons of the vinyl group, which affects the coupling of the spins of the nuclei and electrons and, consequently, the SSCC.



The differences in the constants for the trans-E and cis-Z conformers of 1-phenyl-5-triphenylphosphoniamethylideneimidazolidine-2,4-dione perchlorate can also be explained from these standpoints, since in the first case the great resonance stabilization of the positive charge decreases the effective charge on the phosphorus atom, structurally drawing together the cyclic and protonated forms. The similarity in their electronic spectra is also associated with this.



The decrease in the electron density on the phosphorus atom is less effective in cis-Z isomer VII, since the less favorable (as compared with IX) ylene form X and the more electronegative carbon and oxygen atoms participate in charge stabilization; this is possibly also responsible for the lower value of the observed constant.

EXPERIMENTAL

The UV spectra of solutions of the compounds in methanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in dimethyl sulfoxide (DMSO) were obtained with a BS-467 C spectrometer with tetramethylsilane (TMS) as the internal standard.

2,2,2-Triphenyl-4-(p-bromophenyl)-1,2-$\Delta^{3'}$-oxaphospholeno[4,5-d]-$\Delta^{3'}$-imidazolin-5-one (IIIc). A mixture of 0.52 g (2 mmole) of triphenylphosphine and 0.68 g (2 mmole) of 1-(p-bromophenyl)-5-formyl-4-(1'-pyridinia)imidazole 2-oxide (Ic) was refluxed in 15 ml of acetic acid for 2 h, after which the reaction mixture was cooled and treated with 25-30 ml of ether, and the resulting precipitate was crystallized from isopropyl alcohol to give 0.42 g (54%) of a product with mp 265-267°C. PMR spectrum: 4.91 (1H, d, $=CH-$). Found: C 63.6; H 3.6; Br 14.9; N 5.3; P 5.7%. $C_{28}H_{20}BrN_2O_2P$. Calculated: C 63.8; H 3.8; Br 15.2; N 5.3; P 5.9%.

2,2,2,4-Tetraphenyl-1,2-Δ^3-oxaphospholeno[4,5-d]imidazolin-5-one (IIIa). This compound, with mp 256-260°C (ethanol), was similarly obtained in 56% yield. PMR spectrum: 4.75 ppm (1H, d, $=CH-$). Found: C 73.2; H 5.1; N 6.3; P 6.9%. $C_{28}H_{21}N_2O_2P$. Calculated: C 75.0; H 4.7; N 6.3; P 6.9%.

2,2,2-Triphenyl-1,2-Δ^3-oxaphospholeno[4,5-d]thiazolin-5-one (IIIb). A mixture of 2 g (10 mmole) of 5-formyl-4-(1'-pyridinia)-thiazole 2-oxide (Ib) and 2.62 g (10 mmole) of triphenylphosphine was refluxed for 20-30 min in 30 ml of acetic acid, after which the reaction mixture was cooled, and the product was precipitated by means of 40 ml of ether. The precipitate was crystallized from acetonitrile–dimethylformamide (2:1) to give 2.6 g (67%) of IIIb with mp 257-260°C. PMR spectrum: 7.11 ppm (1H, d, $=CH-$). Found: C 68.2; H 4.9; P 7.8; S 8.3%. $C_{22}H_{16}NO_2PS$. Calculated: C 67.9; H 4.1; P 8.0; S 8.2%.

1-(p-Bromophenyl)-5-triphenylphosphoniamethylideneimidazolidine-2,4-dione Perchlorate (IVc). A 0.52-g (1 mmole) sample of IIIc was dissolved by refluxing in 40 ml of isopropyl alcohol, after which the solution was cooled to room temperature and treated dropwise with 10-15 ml of 57% perchloric acid in the course of 5-10 min. The mixture was refluxed for 20-30 min, cooled to 25°C, and treated with 10-15 ml of ether. The resulting white substance, which had mp 295-297°C, was removed by filtration. PMR spectrum: 5.49 ppm (1H, d, $=CH-$). Found: C 53.5; H 3.5; Br 12.7; Cl 5.5; N 4.5; P 4.9%. $C_{28}H_{20}BrN_2O_2P\cdot HClO_4$. Calculated: C 53.4; H 3.3; Br 12.7; Cl 5.6; N 4.5; P 4.9%.

1-Phenyl-5-triphenylphosphoniamethylideneimidazolidine-2,4-dione Perchlorate (IVa, trans-E Isomer). This compound, with mp 298-300°C (isopropyl alcohol), was similarly obtained. PMR spectrum: 5.47 ppm (1H, d, $=CH-$). Found: C 61.5; H 4.1; Cl 6.6; N 5.4; P 5.4%. $C_{28}H_{21}N_2O_2P\cdot HClO$. Calculated: C 61.2; H 4.0; Cl 6.5; N 5.1; P 5.7%.

1-Phenyl-5-triphenylphosphoniamethylideneimidazolidine-2,4-dione Perchlorate (VII, cis-Z Isomer). A mixture of 0.66 g (30 mmole) of 1-phenyl-4-chloro-5-formylimidazolin-5-one and 0.78 g (30 mmole) of triphenylphosphine was refluxed in 20 ml of acetonitrile for 30 min, after which the reaction mixture was cooled to room temperature and treated with 15 ml of ether. The resulting precipitate was dissolved in 10 ml of distilled water, and the solution was treated dropwise with 10-15 ml of 57% perchloric acid in the course of 5-10 min. The resulting white precipitate of VII was crystallized from isopropyl alcohol to give 1 g (62%) of a product with mp 243-245°C. PMR spectrum: 6.23 ppm (1H, d, $=CH-$). Found: C 63.1; H 4.5; Cl 6.2; P 5.5%. $C_{28}H_{21}N_2O_2P\cdot HClO_4$. Calculated: C 61.3; H 4.0; Cl 6.4; N 5.1; P 5.7%.

1-Phenyl-4-triphenylphosphonia-5-formylimidazole 2-Oxide Perchlorate (Va). A) A mixture of 2.2 g (10 mmole) of 1-phenyl-4-chloro-5-formylimidazolin-2-one and 2.62 g (10 mmole) of triphenylphosphine was refluxed in 30 ml of acetic acid for 30 min, after which the reaction mixture was cooled to 25°C and treated with 25-30 ml of ether until the precipitation of the betaine hydrochloride was complete. This procedure gave 3.32 g (64.6%) of product. The precipitate was then removed by filtration and dissolved in 15 ml of boiling water, and 4-7 ml of 57% perchloric acid was then added until the liberation of perchlorate Va was complete. The crude product contained 23% 1-phenyl-4-triphenyl-phosphonia-5-formylimidazole 2-oxide hydrochloride, which was separated by extraction with 40 ml of isopropyl alcohol. Compound Va was crystallized from acetic acid to give a product with mp 242-245°C in 77% yield. UV spectrum (in methanol), λ_{max} (log ε): 270 (4.0), 277 (4.0), and 377 nm (3.4). Found: C 64.1; H 5.1; Cl 6.5; P 5.7%. $C_{28}H_{21}N_2O_2P\cdot HClO_4$. Calculated: C 61.3; H 4.0; Cl 6.5; N 5.1; P 5.7%.

B) A 2.66-g (10 mmole) sample of perchlorate Ia was dissolved in 40 ml of acetic acid after which 5-6 ml of 57% perchloric acid was added, and 2.62 g (10 mmole) of triphenylphosphine was added to the resulting precipitate. The mixture was refluxed for 3-3.5 h, after which it was cooled to room temperature. The resulting precipitate was removed by filtration and distilled in 20 ml of isopropyl alcohol, and the undissolved Va was crystallized from acetic acid to give 1.78 g (67%) of a product with mp 242-243°C.

LITERATURE CITED

1. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High-Resolution NMR Spectroscopy, Pergamon, Oxford (1965).
2. T. H. Siddal and C. A. Prohaska, J. Am. Chem. Soc., 84, 2502 (1962).
3. R. O. Kochkanyan, S. S. Lukanyuk, T. A. Dmitruk, and N. G. Korzhenevskaya, Zh. Obshch. Khim., 55, 195 (1985).
4. R. O. Kochkanyan, S. S. Radkova, N. L. Klyuev, L. Yu. Petrovskaya, and S. N. Baranov, Khim. Geterotsikl. Soedin., No. 12, 1687 (1978).
5. C. E. Johnson and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958).
6. J. A. Pople and D. P. Santry, Mol. Phys., 8, 269 (1964).
7. T. Schaefer, Can. J. Chem., 40, 1 (1962).

ABSOLUTE CONFIGURATIONS OF DIASTEREOMERIC ESTERS OF 1,4-TETRAHYDROTHIAZINE-3,5-DICARBOXYLIC ACID

A. V. Eremeev, R. Nurdinov, F. D. Polyak,
É. É. Liepin'sh, A. V. Mishnev, M. F. Bundule,
and Ya. Ya. Bleidelis

UDC 547.869.2:548.737:541.634

The reaction of dimethyl 1,4-tetrahydrothiazone-3,5-dicarboxylate with phenyl isocyanate and phenyl isothiocyanate leads to 2,4-dioxo-3-phenyl-9-methoxycarbonyl-7-thia-1,3-diazabicyclo[3.4.0]nonane and its thioxo analog. It is shown that only the trans isomer of the starting diester undergoes the reaction.

The reaction of methyl 1,2-dibromopropionate with L-cysteine methyl ester leads to the formation of a pair of SS and SR diastereomers of dimethyl 1,4-tetrahydrothiazone-3,5-dicarboxylate, which were separated into individual diastereomers by high-performance liquid chromatography (HPLC) [1]. The diastereomers are uncrystallizable liquids, which made it impossible to establish the absolute configuration of each of them by x-ray diffraction analysis. We therefore attempted to obtain crystalline derivatives of 1,4-tetrahydrothiazine-3,5-dicarboxylic acid for the subsequent determination of the absolute configurations by x-ray diffraction analysis.

We have previously shown that the reaction of methyl 1,4-tetrahydrothiazone-3-carboxylate with isocyanates and isothiocyanates leads to the formation of a two-ring system that consists of condensed thiazan and imidazolidine rings [2].

In order to obtain crystalline derivatives of diesters Ia, b we carried out their reaction with phenyl isocyanate and phenyl isothiocyanate; as expected, the corresponding two-ring derivatives were obtained as a result of this reaction. However, instead of the expected diastereomeric mixtures, we isolated monoesters VI and VII in the form of one diastereomer.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1056-1059, August, 1985. Original article submitted November 2, 1983; revision submitted September 3, 1984.

0009-3122/85/2108-0879$09.50