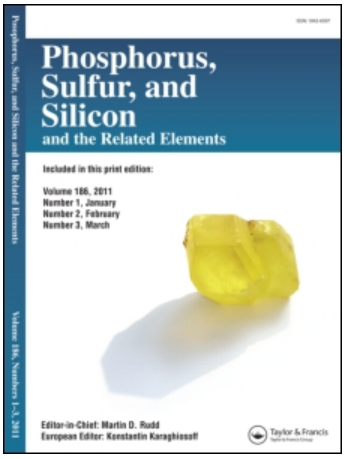

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INVESTIGATION ON THE INFLUENCE OF THE SUBSTITUENTS ON THE DOUBLE BOND STRETCHING VIBRATION FREQUENCIES IN 2,5-DIHYDRO-1,2-OXAPHOSPHOLES

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On the basis of IR spectra the stretching vibration frequencies of the cyclic double bond in some 2,5-dihydro-1,2-oxaphospholes are presented. The influence of the substituents on the double bond spectral characteristics has been investigated.

Key words: 2,5-Dihydro-1,2-oxaphospholes; IR-studies.

INTRODUCTION

In the beginning of the 70s it was found[1] that the interaction of 1,2-alkadienephosphonates with halogens took place with participation of the internal nucleophile (the phosphoryl oxygen) leading to cyclization of the allenephosphonate double bond system to a five-membered ring comprising phosphorus and oxygen. Later it was shown[2] that other electrophilic reagents in reaction with 3-substituted allenephosphonates also lead to 2,5-dihydro-1,2-oxaphosphole derivatives. As a result of the accumulated experimental data a method was established for synthesizing the not easily accessible oxaphosphole derivatives. The infrared spectra of 2,5-dihydro-1,2-oxaphosphole derivatives show that the stretching vibration frequency of the cyclic double bond can be sensibly influenced by the nature of the substituents—an effect not discussed in the literature available.

The intention of the present work is to analyze the influence of the substituents on the stretching vibration frequency of the double bond in differently substituted 2,5-dihydro-1,2-oxaphospholes.

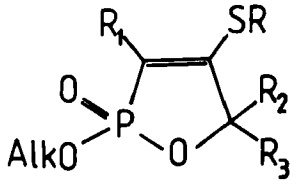
RESULTS AND DISCUSSION

The double bond stretching vibration frequency values $\nu_{C=C}$ for some 2,5-dihydro-1,2-oxaphosphole derivatives are given in the Tables I–IV.

† Author to whom correspondence should be addressed.

TABLE I

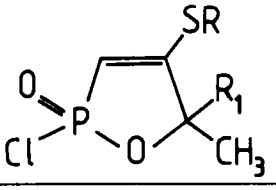
$\nu_{C=C}$ values of 2-alkoxy-4-alkylthio-2,5-dihydro-1,2-oxaphospholes



R	R_1	R_2	R_3	Alk	$\nu_{C=C}$ [cm^{-1}]	Ref.
CH_3, C_2H_5 i-C_3H_7, C_6H_5	H	cyclohexyl		CH_3, C_2H_5 i-C_4H_9	1579–1560	3
CH_3, C_2H_5 i-C_3H_7, C_6H_5	H	CH_3	CH_3, C_2H_5	CH_3, C_2H_5, C_3H_7 i-C_3H_7, C_4H_9	1571–1552	4
CH_3, C_2H_5 i-C_3H_7	H, CH_3	H, CH_3	CH_3, C_3H_7	CH_3, C_2H_5	1610–1552	5

TABLE II

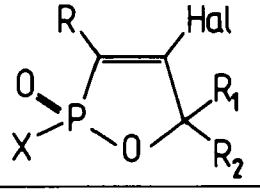
$\nu_{C=C}$ values of 2-chloro-4-alkyl(aryl)thio-2,5-dihydro-1,2-oxaphospholes[6]



R	R_1	$\nu_{C=C}$
CH_3	CH_3	1525
C_2H_5	CH_3	1530
C_3H_7	CH_3	1525
C_4H_9	CH_3	1530
C_6H_5	CH_3	1530
CH_3	C_2H_5	1532
C_3H_7	C_2H_5	1532

TABLE III

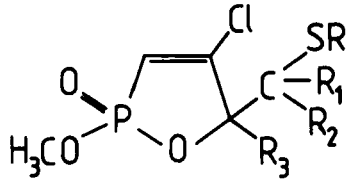
$\nu_{C=C}$ values of 4-halogen-2,5-dihydro-1,2-oxaphospholes



R	Hal	X	R_1	R_2	$\nu_{C=C}$ [cm^{-1}]	Ref.
H	Cl, Br	CH_3O, C_2H_5O, Cl	CH_3	CH_3, C_2H_5 C_9H_7	1595–1573	7
H	Cl, Br	CH_3O, C_2H_5O, i-C_3H_7O, C_3H_7O, i-C_4H_9O, C_4H_9O	cyclohexyl		1600–1595	8
H	Cl, Br	CH_3O, C_2H_5O i-C_3H_7O, C_3H_7O	CH_3	CH=CH_2	1598–1590	9
H	Cl	Cl, CH_3O, C_2H_5O, C_3H_7O, C_4H_9O, C_5H_6	H CH_3	CH_3, C_2H_5 C_3H_7	1595–1582	10, 11
CH=CH_2	Cl, Br	CH_3O, C_2H_5O i-C_3H_7O, C_4H_9O	CH_3	CH_3	1595–1588	12

TABLE IV

$\nu_{C=C}$ values of 4-chloro-2,5-dihydro-1,2-oxaphospholes[13]



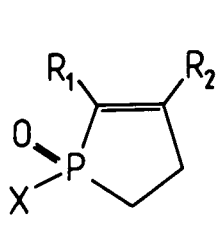
R	R_2	R_3	R	$\nu_{C=C}$
H	H	CH_3	CH_3	1584
H	H	CH_3	$C_6H_4CH_3$	1586
H	CH_3	C_2H_5	C_6H_5	1585
CH_3	CH_3	CH_3	$C_6H_4CH_3$	1575

According to Bellamy,[14] $\nu_{C=C}$ of the five-membered cyclic alkenes is usually observed between 1686–1611 cm^{-1} in dependence on the number and the type of the substituents. In the Tables I–IV one can see that for 2,5-dihydro-1,2-oxaphosphole derivatives $\nu_{C=C}$ is considerably lower. This reduction is probably due to the additional cyclic tension created by the ring heteroatoms but this assumption does not allow a full explanation of the spectral data.

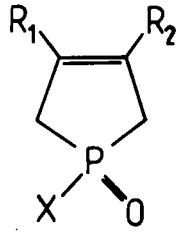
We suppose that for some 2,5-dihydro-1,2-oxaphosphole derivatives a conjugation is possible between the double bond π-electrons and the *d*-orbitales of the P-atom. This conjugation is the reason for the considerable reduction of $\nu_{C=C}$ in comparison with reported[14] data. We made this assumption on the strength of the following:

(i) The investigations[15] of some vinylphosphonic acids to establish if there is a conjugation between vinyl groups and the phosphorus atom prove that such conjugation exists. It provokes an insignificant shift of the P=O band ($\Delta\nu_{P=O}$ = 4 cm^{-1}) but the C=C frequency reduction is 20 cm^{-1} (it is interesting to note that the same shift is usually observed in the case of the double bond-carbonylic group conjugation).

(ii) As vinylphosphonic acids are not cyclic compounds, we compared the IR spectra of some cyclic analogs of 2,5-dihydro-1,2-oxaphosphole with general formulas:[16]



A

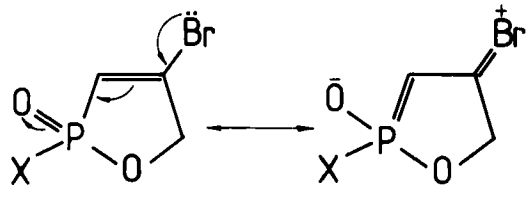


B

where X = Hal, OAlk and R_1, R_2 = H, Alk.

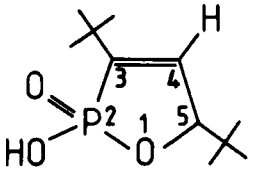
The C=C band of compounds **A** (with the phosphoryl group next to the double bond) for all cases was more intensive and appeared at lower frequency than the C=C band of compounds **B**. Hence, in case **A** the C=C double bond and the phosphoryl group are conjugated and the effect is not due just to the influence of the heavier P-atom.

(iii) This supposition is confirmed by the C^{13}NMR spectra of 1,2-oxaphospholes with Br-atom in position 4, showing $p-d_\pi$ resonance:[17]



Scheme 1

(iv) X-ray investigations[18] on the compounds of the type:

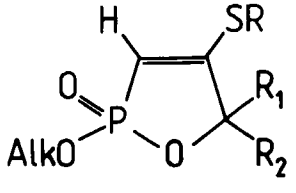


have shown that the five-membered ring is envelope shaped and slightly twisted with the $P_2O_1C_5$ plane tipped 0.66° away from the $C_5C_4C_3P_2$ plane. We suppose that in 2,5-dihydro-1,2-oxaphosphole derivatives synthesized by us such favourable arrangement of the double bond carbon atoms and the phosphorus is present which allows the commented conjugation to be accomplished.

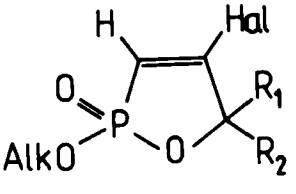
Now we will successively consider the influence of the substituents at different positions in the ring on $\nu_{C=C}$ of 2,5-dihydro-1,2-oxaphosphole derivatives.

INFLUENCE OF C-4 SUBSTITUENTS

In order to consider the influence of the substituents at C-4, two groups of compounds will be compared:

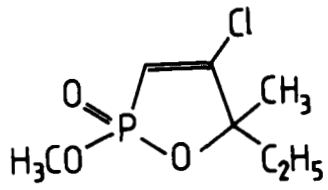


$R = CH_3$, C_2H_5, i-C_3H_7; $R_1 = CH_3$; $R_2 = CH_3$, C_2H_5
Alk = CH_3, i-C_3H_7
$\nu_{C=C} = 1572 - 1568\ cm^{-1}$

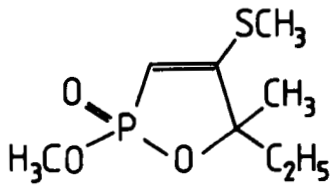


Hal = Cl, Br; Alk = CH_3, C_2H_5
$R_1 = CH_3$; $R_2 = CH_3$, C_2H_5, C_3H_7
$\nu_{C=C} = 1595 - 1583\ cm$

The C=C band of 4-halogen substituted derivatives was observed at higher frequencies than $\nu_{C=C}$ of 4-alkylthio derivatives. Let us compare the following two compounds:

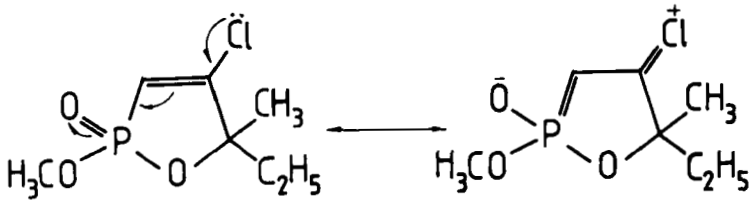


$\nu_{C=C} = 1595\ cm^{-1}$

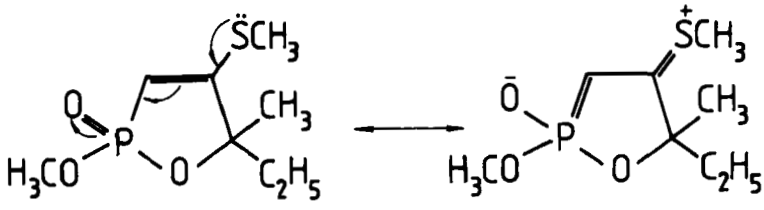


$\nu_{C=C} = 1572\ cm^{-1}$

The substituent masses and the force-constants of C—Cl and C—S bonds indisputably have an effect on the value of $\nu_{C=C}$, but in our view the influences of the induction and mesomeric effects of the substituents[19] on the electronic density of the double bond are decisive. Otherwise one could not explain why the substitution of the alkylthio group with the lighter chlorine provokes a shift of C=C band to higher frequencies.



Scheme 2



Scheme 3

$$-I^{Cl} > -I^{SCH_3}$$

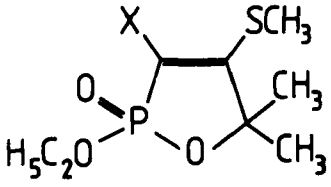
$$+M^{Cl} < +M^{SCH_3}$$

In the first case, the negative induction effect of chlorine compensates somewhat for the conjugation of the double bond with the phosphoryl group. However, the total electronic distribution for the second compound is determined by the positive mesomeric effect of alkylthio group. This leads to more expressive polarization of the double bond and to lower frequency than $\nu_{C=C}$ of 4-Cl substituted compound.

INFLUENCE OF C-3 SUBSTITUENTS

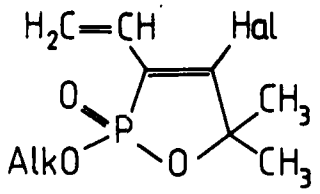
Among the 2,5-dihydro-1,2-oxaphospholes synthesized by us there were no 3-substituted compounds without substituent at C-4 position. The spectra of several 4-methylthio-2,5-dihydro-1,2-oxaphospholes with various C-3 substituents were compared. The $\nu_{C=C}$ values for these compounds are given in Table V.

TABLE V

	X	H	CH_3	Cl	$CH=CH_2$	C_6H_5
	$\nu_{C=C}$	1561	1601	1547	—	—

The spectra of 3-vinyl and 3-phenyl compounds had several bands with very low intensity in the range 1600–1550 cm^{-1} and it was impossible to identify the band of the cyclic double bond. From the Table V one can see that the substitution of C-3 hydrogen by methyl group shifts the C=C band 40 cm^{-1} to higher frequencies. This should be expected having in mind that a new C—C bond was formed which ought to be stretched and shrunk during the vibration of the double bond. The positive induction effect of the methyl group also influences $\nu_{C=C}$. The 3-Cl-substituted derivative showed the lowest C=C frequency which could be undoubtedly linked with the negative induction effect of chlorine.

Another group of compounds has been synthesized, with the general formula:



Hal = Cl, Br

Alk = CH_3, C_2H_5, i-C_3H_7, C_4H_9.

In the spectra of these compounds, unlike the spectra of 4-methylthio derivatives, two bands in the range 1636–1588 cm^{-1} were clearly observed. The band with higher frequency was caused by the vinyl group stretching vibration and the lower frequency band was due to the stretching vibration of the double bond in the ring. The $\nu_{C=C}^{CH=CH_2}$ values (Table VI) indicate the vinyl group is conjugated with the ring double bond. However, this conjugation (although confirmed by the $\nu_{C=C}^{CH=CH_2}$ values) does not affect $\nu_{C=C}^{ring}$ (Table VI and Table VII).

The values of $\nu_{C=C}^{ring}$ for both unsubstituted at C-3 and 3-vinyl-substituted compounds are in the interval 1595–1590 cm^{-1}.

TABLE VI

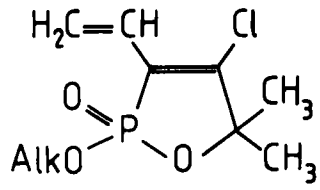
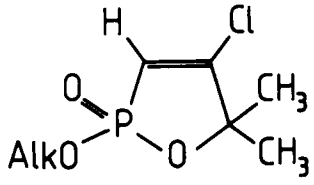
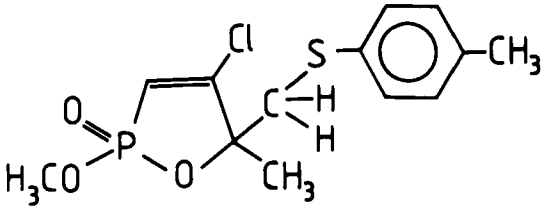
	Alk	CH_3	C_2H_5	i-C_3H_7	n-C_4H_9
	$\nu^{CH=CH_2}$	1632	1633	1636	1635
	$\nu^{ring}_{C=C}$	1592	1594	1595	1594

TABLE VII

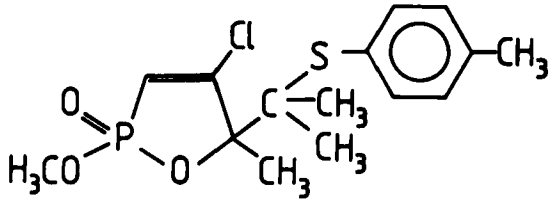
	Alk	CH_3	i-C_3H_7	n-C_4H_9
	$\nu^{ring}_{C=C}$	1595	1590	1592

INFLUENCE OF C-5 SUBSTITUENTS

It can be supposed that the enlargement of C-5 substituents would lead to steric repulsion between them, which in its turn would affect the conjugation and would change $\nu_{C=C}$ value. In fact, this effect was noticed in the compounds of the type:

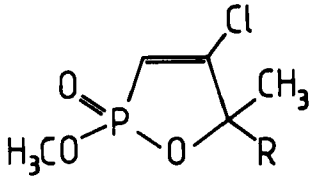


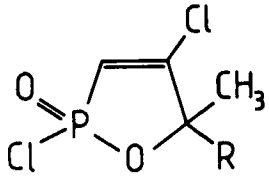
$\nu_{C=C} = 1587\ cm^{-1}$ $\Delta\nu_{C=C} = 12\ cm^{-1}$



$\nu_{C=C} = 1575\ cm^{-1}$

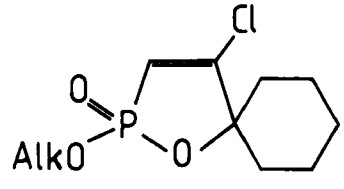
However, in many cases the size changes of C-5 substituents did not affect essentially $\nu_{C=C}$ values. For instance:

	R	CH_3	C_2H_5	$CH(CH_3)_2$	cyclo-hexyl
	$\nu_{C=C}$	1595	1595	1595	1598

	R	CH_3	C_2H_5	$CH(CH_3)_2$
	$\nu_{C=C}$	1583	1587	1586

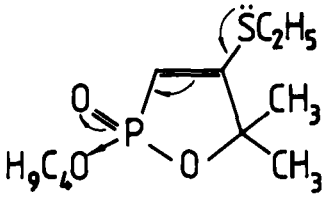
INFLUENCE OF THE SUBSTITUENTS AT THE PHOSPHORYL GROUP

The investigation of the spectra of compounds with various alkoxygroups showed that the type of Alk did not change substantially the position of C=C band. For example:

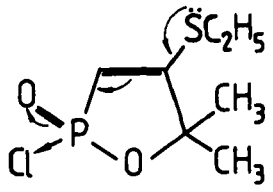
	Alk	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9
	$\nu_{C=C}$	1598	1595	1598	1600	1599

The replacement of alkoxygroup by chlorine leads to reduction of the double bond stretching vibration frequency probably due to the influence of the induction effect of the strongly electronegative chlorine. $\Delta\nu_{C=C}$ depends on the substituent at C-4 too. In 4-alkylthio substituted derivatives the electronic effects of the substituents at P=O and at C-4 act in one and the same directions while in 4-Cl derivatives they act in the opposite directions and compensate each other to

a certain degree:

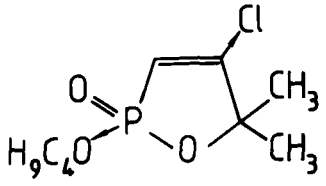


$\nu_{C=C} = 1560\ cm^{-1}$

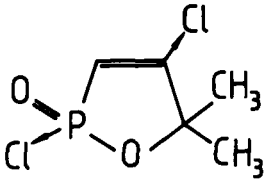


$\nu_{C=C} = 1530\ cm^{-1}$

$\Delta\nu_{C=C} = 30\ cm^{-1}$



$\nu_{C=C} = 1592\ cm^{-1}$



$\nu_{C=C} = 1583\ cm^{-1}$

$\Delta\nu_{C=C} = 9\ cm^{-1}$

As a result the cyclic double bonds in the 4-Cl derivatives are less polarized and the corresponding frequencies are higher than in 4-alkylthio derivatives.

CONCLUSIONS

By comparing our IR-data with the literature, the following conclusions can be made:

(i) In some 2,5-dihydro-1,2-oxaphosphole derivatives a conjugation is accomplished between π-electrons of the cyclic double bond and the phosphorus *d*-orbitales. The free electronic pairs of the substituents at the double bond also take part in this conjugation.

(ii) The values of $\nu_{C=C}$ strongly depend on the influence of the total electronic effects (induction and mesomeric) of C-3 and C-4 substituents.

(iii) The type of the substituents of C-5 in most cases does not affect substantially $\nu_{C=C}$ values.

(iv) The stretching vibration frequency depends on the type of the substituent at the phosphoryl group. The exchange of alkoxy-group by electronegative chlorine atom shifts C=C band to lower frequencies.

EXPERIMENTAL

The IR spectra (CCl_4 solutions and neat) were carried out on a UR-10 and SPECORD 75 IR spectrophotometer (Carl Zeiss Jena, GDR).

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