BASICITY OF FUCHSONES. INFRARED STUDY OF THE ν(OH) STRETCHING VIBRATION IN PHENOL-FUCHSONE COMPLEXES*

Jiří VELEK, Bohumír KOUTEK, Lubomír MUSIL, SoŇa VAŠÍČKOVÁ and Milan SOUČEK

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6

Received December 24th, 1980

The hydrogen bond complexes involving phenol and carbonyl oxygen of 2- and 2,6-substituted fuchsones *I* and *II* have been studied by infrared spectroscopy in tetrachlorethylene solution. Basicities expressed as complexation enthalpies, frequency shifts and integrated intensities of the ν(OH) stretching vibrations are reported. A linear relationship was found between the frequency shift and the hydrogen bond energy. Statistical analysis of linear free energy relationships for fuchsones *I* and *II* proved the significancy of steric factor in transmission of electronic substituent effect.

Numerous experimental studies have shown that carbonyl containing compounds can act as Lewis bases in a variety of situations. These include the formation of hydrogen-bonded complexes[1], charge-transfer complexes[2], protonation in superacids at low temperatures[3] and the formation of protonated species in the gas phase[4]. It is known[5] that compounds in which the carbonyl group is directly connected to a cyclic polyene system have demonstrated an unusually strong basic character of the carbonyl group. Although the Lewis basicity of the carbonyl group has been investigated, only meager experimental results for cyclic conjugated carbonyl compounds are available[6,7].

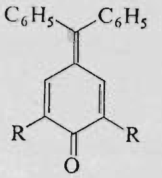
Quinone methides[8], which represent a class of compounds containing a stabilised cyclic arrangement of double bonds, are characterized by conjugation which formally can be classified as crossed. The sensitivity of physico-chemical properties of quinone methide moiety to substitution[9] and especially to the structural changes of the carbonyl group[10] environment makes these compounds suitable models for the study of structural effects on the basicity of their carbonyl group. The most commonly used criterion for the presence of hydrogen bonding provides infrared spectroscopy[11] and the infrared shifts $\Delta\nu(OH) = \nu(OH) - \nu_{max}(OH)$ (where ν(OH) and ν_{max}(OH) are the free and bonded hydroxyl stretching wavenumbers, respectively) are frequently used as a measure of carbonyl group basicity. We use the term basicity

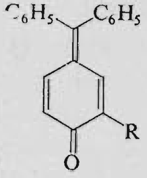
---

* Part XXI in the series Quinone Methides and Fuchsones; Part XX: This Journal *46*, 1775 (1981).

in its broadest sense, the ability of an electron donor to donate electron density to an electron acceptor, which is conveniently expressed as the enthalpy of reaction.

In this communication we report a study of the thermodynamic (enthalpy of complex formation) and spectroscopic (frequency shifts and intensities of the ν(OH) vibration) properties of hydrogen bonded complexes involving phenol and substituted fuchsones *I* and *II*.





Ia; R = H
Ib; R = CH_3
Ic; R = C_2H_5
Id; R = t-C_4H_9
Ie; R = Br
IIf; R = OCH_3

IIa; CH_3
IIb; C_2H_5
IIc; i-C_3H_7
IId; t-C_4H_9
IIe; Br
IIf; OCH_3

EXPERIMENTAL

The fuchsones *I*—*II* were prepared by the known procedures and their physico-chemical constants agreed with the reported values[12].

Infrared spectra were measured on Perkin–Elmer 580 spectrophotometer. Temperature of the solution was measured with a thermistor immersed in the cell (accuracy ± 1°C). When necessary the spectra have been recorded on an extended scale. The formation constants (*K*) have been calculated from the absorbance data of the free phenol taken at 3 612 cm^{-1}; the phenol concentration was about 10^{-3} mol l^{-1} in order to prevent self-association and the concentration of fuchsones ranged from 10^{-1} to 10^{-2} mol l^{-1}. In this limited range the *K* value does not depend on concentration. The reported values resulted from the separate determinations. All measurements were performed with tetrachloroethylene as solvent at temperatures of 303, 323 and 343 K. The frequency shifts, $\Delta\nu$(OH), which are defined as the frequency difference between the absorption maxima for the free and complexed phenol were determined at 298 K at concentrations of phenol equal to 0·005 mol l^{-1} and that of fuchsone equal to 0·12 mol l^{-1}; for this limited range, the $\Delta\nu$(OH) values were practically concentration independent and, consequently, no extrapolation method has been used. Results of the measurements were analysed using the programme for multiple regression (Hewlett–Packard Standard Statistics Pac No 2), on a Hewlett–Packard 9830 A Calculator.

RESULTS AND DISCUSSION

The various spectroscopic methods which have been used to obtain thermodynamic data for hydrogen-bonded systems are based upon an examination of changes in the spectrum of the equilibrium mixture when compared to the spectra of phenol as an acid and fuchsone as a base. IR spectroscopy is the most important method because of the great sensitivity of vibrational modes to the presence of hydrogen bonds. A great deal of attention[13] has been paid to $\nu(OH)$ stretching vibrations; in the moderately hydrogen-bonded systems ($\nu_{max}(OH) = 3\,400 - 2\,400\,cm^{-1}$) a complex $\nu(OH)$ band is observed. The $\nu(OH)$ bands of phenol associated to fuchsones *I* and *II* are broad and unsymmetrical. Hydrogen-bond parameters and some other spectral characteristics of phenol complexes with fuchsones are listed in Table I. The infrared shifts $\Delta\nu(OH)$ which are measured traditionally at the point of maximum absorption represent a composite quantity. Though band deconvolution might be helpful only if the number and type of contributing bands are known. But keeping in mind that the more shifted band (attributed to a n-complex[6,14]) is generally more intense, or that in some cases the component bands are located near same frequency, thereby leading to almost symmetrical bands, apparent maxima may furnish $\Delta\nu(OH)$ data of good reliability for establishing the affinity of lone pair toward a proton donor in a set of related compounds. The enthalpies of adduct formation for a series of substituted fuchsones *I* and *II* have been determined and are summarized with other thermodynamic parameters in Table II. In all cases equilibrium constants, enthalpies and also the $\Delta\nu(OH)$ values decrease with the increase in the bulkiness of the *ortho* substituents. It should be pointed out that $\Delta\nu(OH)$ is related[15] to the magnitude of the splitting of the vibrational levels or to the barrier height in the relevant double minimum potential. Generally, the lower is the barrier height, the greater is the energy of the hydrogen bond O—H···O, since a decrease in barrier height is accompanied by a lowering of the hydrogen bond distance $R(O—H\cdots O)$. The value of R can be calculated by the Lippincott–Schoeder potential function[16]. The R distances for complexes of phenol with fuchsones *I* and *II* are estimated from the relation between R and $\Delta\nu(OH)$ (ref.[16]) and are listed in Table III. The examination of the data shown in Table III reveals that $\Delta\nu(OH)$ also increases with a decrease in the barrier height, because the frequency shift and R distance (or the force constant) vary proportionally. The values of entropy change listed in Table II also support these considerations; the steric effect of the *ortho* substituents causes an increase of $R(O—H\cdots O)$ distance in hydrogen-bonded complex so that the rotational and vibrational movement of the complex is to some extent, less restricted. It follows that steric effects could influence not only the enthalpy but also the entropy changes associated with the formation of the hydrogen-bonded complex.

In spite of being a controversial topic[17,18] the existence of some kind of relationship between frequency shift and complexation enthalpy (Badger–Bauer rule) is a well known fact[19]. For the complexes of phenol with fuchsones *I* and *II* the following relation holds:

$$-\Delta H = 0{\cdot}019\,\Delta\nu(OH) + 1{\cdot}35\,, \quad n = 11,\ r = 0{\cdot}948,\ s = 1{\cdot}8\,. \qquad (1)$$

The most deviating point in this correlation belongs to fuchsone *Id*, substituted in positions 2 and 6 by bulky tert-butyl groups. Exclusion of this point leads to

$$-\Delta H = 0{\cdot}096\,\Delta\nu(\mathrm{OH}) + 5{\cdot}08\,, \quad n = 10,\ r = 0{\cdot}991,\ s = 0{\cdot}6\,. \qquad (2)$$

The acceptable correlation coefficient as well as the reasonable value of the intercept, give support to the linearity of relationship between $\Delta\nu(\mathrm{OH})$ shifts and enthalpies in our set of substituted fuchsones *I* and *II*. It must be remembered that the experimental $-\Delta H$ values deduced from the variation of the overall complexation constants with temperature roughly correspond to the enthalpy of the strongest $n\sigma$ bond but

TABLE I

Spectral parameters (cm^{-1}) of phenol complexes with fuchsones *I* and *II*

Compound	$\nu_{max}(\mathrm{OH})$	$\Delta\nu(\mathrm{OH})$	$\nu_{1/2}$	$(\nu^2 - \nu_{max}^2)^{1/2}$	$\nu(\mathrm{C{=}O})^a$	$2\nu(\mathrm{C{=}O})$
Ia	3 280	320	155	1 513	1 627	3 263 3 240 sh 3 220
Ib	3 340	272	97	1 375	1 615	3 222
Ic	3 350	262	96	1 360	1 603	3 210
Id	3 410	202	48	1 191	1 606	3 208 sh 3 245
Ie	3 450	162	48	1 070	1 643	3 281
If	3 377	235	80	1 281	1 645	3 290 sh 3 270
IIa	3 330	282	120	1 399	1 621	3 233 sh 3 255
IIb	3 355	257	95	1 338	1 618	3 212 sh 3 232
IIc	3 330	282	120	1 399	1 615	3 224
IId	3 290[b]	320[b]	160[b]	—	1 614	3 221 sh 3 245
IIe	3 407	205	76	1 199	1 630	3 259
IIf	3 355	257	94	1 338	1 631	3 270

[a] Data from ref.[10]; [b] owing to the unusual broadness of the band the uncertainty in the $\Delta\nu(\mathrm{OH})$ was too high and these data were excluded from subsequent calculation.

TABLE II

Thermodynamic data of phenol complexes with fuchsones *I* and *II*

Compound	$-\Delta H$ kJ mol^{-1}	$-\Delta S$ J K^{-1} mol^{-1}	K, l mol^{-1}		
			343 K	323 K	303 K
Ia	36·8	83·7	9·9	21·5	52·1
Ib	31·8	96·3	6·2	12·5	27·5
Ic	30·1	78·1	6·9	25·5	65·4
Id	18·8	50·2	1·4	2·1	3·2
Ie	20·5	50·2	3·7	5·7	9·4
If	28·0	79·5	6·1	12·2	40·7
IIa	32·2	83·7	7·9	16·5	38·2
IIb	30·8	75·4	7·3	14·9	29·6
IIc	31·4	72·6	7·8	27·7	70·4
IIe	27·5	61·8	4·5	19·9	50·2
IIf	31·8	71·7	6·3	12·1	24·3

TABLE III

Comparison of frequency shifts, complexation enthalpies and *R* distances for the phenol–fuchsone complexes

Fuchsone	$\Delta\nu$(OH)	$-\Delta H$	R^a
Ia	320	36·8	2·50
Ib	272	31·8	2·88
Ic	262	30·1	2·89
Id	202	18·8	2·94
Ie	162	20·5	2·98
If	235	28·0	2·91
IIa	282	32·2	2·87
IIb	257	30·9	2·89
IIc	282	31·4	2·87
IIe	205	27·5	2·93
IIf	268	31·8	2·88

[a] In units 10^{-8} cm.

are somewhat lowered as a consequence of the simultaneous occurrence of $\sigma\pi$ complexes[20]. It follows, that the true $-\Delta H$ value relative to the formation of OH···O bonds must be somewhat higher and this can slightly affect the coefficients of the Badger–Bauer relation. According to the theory of Ratajczak and Orville-Thomas[21] it is more advantageous to plot the enthalpy, $-\Delta H$, *versus* $(\nu^2 - \nu^2_{\max})^{1/2}$ rather than against $\Delta\nu(\mathrm{OH})$. To discuss this point, we should remember that this plot enables us to determine, at least in principle, the value of ΔH_0 (or W_0 in the theory of Mulliken) (Eq. (*3*)).

$$-\Delta H = C(\nu^2 - \nu^2_{\max})^{1/2} + \Delta H_0\,, \tag{3}$$

where C value includes parameters such as ionization potential of the donor and electronaffinity of the acceptor. Application of Eq. (*3*) on our data leads to

$$-\Delta H = 0{\cdot}042(\nu^2 - \nu^2_{\max})^{1/2} + 18{\cdot}9\,, \quad n = 10,\ r = 0{\cdot}985,\ s = 0{\cdot}8\,. \tag{4}$$

It is clear that the dependence is approximately linear and should afford a reasonable value of ΔH_0. But the rationalization of the value of the intercept of Eq. (*3*) is not so straightforward as the original proposal that the W_0 term of the Mulliken theory does not vary with the strength of the complex, is certainly not valid[22].

The complexation of molecules substantially increases the intensity of $\nu(\mathrm{OH})$ infrared band and this intensification may be considered as one of the most fundamental spectral characteristics[21]. The intensity of an IR band is not a ground state property. It is theoretically proportional to the square of quantity, $\partial\mu/\partial r$, known as the dipole transition moment as in

$$A = \frac{N}{3\,.\,10^3 c^2 \mu_r}\left(\frac{\partial\mu}{\partial r}\right)^2, \tag{5}$$

where r is the OH distance, μ_r the reduced mass of the OH vibrator and N the Avogadro number. The dipole transition moment is the rate of change of dipole moment,

TABLE IV

Intensity data of the $\nu(\mathrm{OH})$ band for phenol complexes with fuchsones *I* and *II*

Fuchsone	*Ia*	*Ib*	*Ic*	*Id*	*Ie*	*If*	*IIa*	*IIb*	*IIc*	*IIe*	*IIf*
$A\,.\,10^{-4}$ [a]	11·25	6·85	7·62	5·27	3·31	6·28	8·67	4·02	7·71	2·57	3·79
$\Delta A^{1/2}\,.\,10^{-2}$ [b]	3·31	2·56	2·76	2·23	1·04	2·45	2·90	1·94	2·73	1·52	1·88

[a] $\mathrm{l\,mol^{-1}\,cm^{-2}}$; [b] $\mathrm{l^{1/2}\,mol^{1/2}\,cm^{-1}}$.

μ, with respect to the relevant normal coordinate. Table IV lists the values of the integrated intensity along with the square root of the intensity increment $\Delta A^{1/2}$. The theory of Rassadin and Ioganse[23], which predicts a linear correlation between the enthalpy of complex formation and the square root of the intensity increment, is illustrated by the following relation:

$$-\Delta H = 0{\cdot}06\,\Delta A^{1/2} + 15{\cdot}5\,, \quad n = 10,\ r = 0{\cdot}917,\ s = 2{\cdot}04\,. \qquad (6)$$

The origin of intensity enhancement has been discussed[24] and obviously results from the superposition of different effects (electrostatic, charge transfer and polarization) which are difficult to separate, but as follows from the inspection of the Table IV the integrated intensity as well as an intensity increment decrease with the increase in the bulkiness of the *ortho* substituents of fuchsones *I* and *II*.

We have recently shown[10] that the influence of substituents in positions 2- and 6- on frequencies and integrated intensities of carbonyl stretching vibrations in fuch-

TABLE V

Statistical evaluation of equation (*7*), (*8*), (*9*) ($P = \Delta\nu(\mathrm{OH})$) for fuchsones *I* and *II*

System	ϱ_I	ϱ_R	ϱ_S	P_O	R^c F^d	$F(\varrho_I)$ $t(\varrho_I)$	$F(\varrho_R)$ $t(\varrho_R)$	$F(\varrho_S)$ $t(\varrho_S)$
I + *II*[a]	−105·41	−19·61	−47·67	300·8	0·958 26·12	387·0 5·9	0·03* 0·8*	39·6 6·3
I + *II*[a]	− 97·18	—	−46·71	304·0	0·954 40·62	40·52 6·8	—	40·71 6·3
I + *II*[a]	73·26	18·15	—	278·2	0·805 2·06	0·96 0·98	0·05* 0·22*	—
I[b]	− 98·48	—	−52·82	317·82	0·998 468·9	375·1 22·4	—	562·7 23·7
I[b]	− 74·23	20·66	—	262·3	0·638 1·03	2·01 1·05	0·04* 0·21*	—
II[b]	−126·51	—	−79·36	317·8	0·937 10·78	13·62 3·9	—	7·94 2·8
II[b]	−141·95	−19·52	—	278·8	0·747 1·89	3·7 1·69	0·02* 0·16*	—

[a] $n = 12$; [b] $n = 6$; [c] multiple correlation coefficient; [d] total F-test (the asterisk denotes factors with the significance level <95%).

sones *I* and *II* is quite complex and an investigation of its nature requires separation of the steric and proximity electronic component. We have shown that wavenumber and integrated intensity of the carbonyl band decrease with increasing van der Waals volume of the substituents and the contribution of steric effect to the total trans-

TABLE VI

Statistical evaluation of equations (*7*), (*8*), (*9*) ($P = -\Delta H$) for fuchsones *I* and *II*

System	ϱ_I	ϱ_R	ϱ_S	P_O	R^c F^d	$F(\varrho_I)$ $t(\varrho_I)$	$F(\varrho_R)$ $t(\varrho_R)$	$F(\varrho_S)$ $t(\varrho_I)$
$I + II^a$	−7·97	−0·60	−7·14	36·2	0·978 51·87	29·5 5·3	2·14* 0·29*	123·98 11·1
$I + II^a$	−7·71	—	−7·11	36·3	0·978 87·78	33·30 6·6	—	142·26 11·92
$I + II^a$	−6·25	−0·42	—	34·2	0·810 1·85	38·4 6·2	0·30* 0·09*	—
I^b	−8·26	—	−7·72	37·6	0·991 84·06	25·38 6·61	—	142·73 11·94
I^b	−7·15	−0·36	—	33·2	0·765 0·92	32·6 5·8	0·22* 0·05*	—
II^b	−7·61	—	−8·55	36·5	0·971 25·22	18·55 3·89	—	31·90 5·64
II^b	−7·41	−0·51	—	35·8	0·715 0·86	18·34 3·54	0·24* 0·06*	—

[a] $N = 12$; [b] $N = 6$; [c] multiple correlation coefficients; [d] total F-test (the asterisk denotes factors with the significance level <95%).

TABLE VII

Relative contributions of inductive and steric effects calculated from data in Tables *V* and *VI*

System	Δν(OH)		−Δ*H*	
	%I	%S	%I	%S
I + *II*	55	45	38	62
I	45	55	32	68
II	65	35	51	49

mission is higher for 2,6-disubstituted than for 2-monosubstituted fuchsones. Interesting behaviour of fuchsone substituted in position 2 by a hydroxyl group has prompted us, that the hydrogen-bonding ability might prove to be even more sensitive probe in evaluation of *ortho* effect on the properties of fuchsones.

The general approach is based on comparison of the equation (*7*)

$$P - P_0 = \varrho_I \sum\sigma_I + \varrho_R \sum\sigma_R + \varrho_S \sum\nu \qquad (7)$$

with its two-parameter analogues (*8*) and (*9*),

$$P - P_0 = \varrho_I \sum\sigma_I + \varrho_R \sum\sigma_R\,, \qquad (8)$$

$$P - P_0 = \varrho_I \sum\sigma_I + \varrho_S \sum\nu\,, \qquad (9)$$

where P is the studied property in energy units and the meaning of other parameters is obvious. Statistical analysis of the equations (*7*), (*8*) and (*9*) for all studied compounds and for separately correlated mono and disubstituted fuchsones (*I* and *II*, respectively) is summarized in Table V for $P = \Delta\nu(\mathrm{OH})$ and in Table VI for $P = \Delta H$. Statistical significance of the single regression coefficients was tested at a significance level given by $\alpha = 0{\cdot}05$ for $N - q - 1$ degrees of freedom (where N is the number of data and q is the number of regressors). The examination of the data shown in Table V and VI reveals, that the resonance term $\varrho_R\sigma_R$ is according to F as well as t-tests invariably statistically insignificant, regardless of the choice of σ_R constants set. The relative importance of inductive and steric effects can be estimated quantitatively by the comparison of percentage contributions I and S to the observed variation of the property as calculated according to Swain–Lupton procedure[25]. The contribution of inductive effects is found in all cases to be significant and ranges between 65% and 32% (Table VII). However it is obvious, that the steric contribution to total transmission is more pronounced than described earlier[10].

Different substituent constants have been derived[26-28] in order to cope with experimental data involving wide variation in steric contributions, but a set of steric constants of universal applicability is still not available. It follows, that the best fit is still the most used criterion and the LFER equations are selected by the method of trial and error. In this report we use steric parameter[29] ν $(\nu = r_v^x - r_v^H)$ where r_v is the van der Waals volume, assuming that r_v can be taken as a measure of the steric effect. We have also compared out results with a recently proposed scale[30] of steric parameters S^0, but our data are with this set of steric constants only poorly correlated.

An analysis of steric contribution to total transmission requires a splitting of overall correlation into two partiall ones, according to the substituent position. The examination of percentage contribution of steric effects shown in Table VII reveals that the influence of steric effect is for disubstituted fuchsones *I* either significant ($P = \Delta\nu(OH)$) or heavily dominating ($P = -\Delta H$). For monosubstituted fuchsones *II* is the steric effect in both cases less pronounced.

We can thus summarize that the thermodynamic data obtained in this work corroborate our original assumption about a strong basic character of fuchsone carbonyl group. We have also established a reciprocal relationship between both the thermodynamic (K, $-\Delta H$) and spectroscopic ($\Delta\nu(OH)$) data and steric demands of the *ortho* substituents. The statistical approach used in this work has proved to be satisfactory for interpretation of the *ortho*-effect in 2-substituted and 2,6-disubstituted fuchsones using infrared shifts and complexation enthalpies.

REFERENCES

1. Pimentel G. C., McClellan A. L.: *The Hydrogen Bond.* Reinhold, New York 1960.
2. Foster J., Keefer R. M.: *Molecular Complexes in Organic Chemistry.* Holden-Day, San Francisco 1964.
3. Olah G. A., Calin M.: J. Amer. Chem. Soc. *90*, 938 (1968).
4. Long J., Munson B.: J. Amer. Chem. Soc. *95*, 2427 (1973).
5. Lloyd D.: *Carbocyclic Non-Benzoid Aromatic Compounds.* Elsevier, Amsterdam 1966.
6. Fritzsche H.: Spectrochim. Acta, Part A, *21*, 799
7. Bostwick D., Henneike H. F., Hopkins H. P.: J. Amer. Chem. Soc. *97*, 1505 (1975).
8. Wagner H. U., Gompper R. in the book: *Chemistry of the Quinonoid Compounds* (S. Patai, Ed.), Part 2, p. 1145. Interscience, London 1974.
9. Koutek B., Musil L., Pavlíčková L., Vašíčková S., Souček M.: This Journal *44*, 2970 (1979).
10. Velek J., Koutek B., Musil L., Vašíčková S., Souček M.: This Journal *46*, 873 (1981).
11. Joesten M. D., Schaad L. J.: *Hydrogen Bonding.* Dekker, New York 1974.
12. Grünanger P. in the book: *Methoden der organischen Chemie* (*Houben-Weyl*) (Ch. Grundmann, Ed.) Vol VII/3b, p. 395. Thieme, Stuttgart 1979.
13. Ref. 11., p. 2.
14. Joris L., Schleyer P. von R.: J. Amer. Chem. Soc. *90*, 4599 (1968).
15. Singh S., Rao C. N. R.: J. Amer. Chem. Soc. *88*, 2142 (1966).
16. Lippincott E. R., Schroeder R.: J. Chem. Phys. *23*, 1009 (1955).
17. Badger R. M., Bauer S. H.: J. Chem. Phys. *5*, 839 (1939).
18. Singh S., Murthy A. S. N., Rao C. N. R.: Trans. Faraday Soc. *62*, 1056 (1966).
19. Joesten M. D., Drago R. S.: J. Amer. Chem. Soc. *84*, 3817 (1962).
20. Yoshida Z. I., Ishibé N.: Bull. Chem. Soc. Jap. *42*, 3259 (1969).
21. Ratajczak H., Orwille-Thomas W. J., Rao C. N. R.: J. Chem. Phys. *17*, 197 (1976).
22. Zeegers-Huyskens T.: Bull. Soc. Chim. Belg. *86*, 823 (1977).
23. Rassadin B. V., Iogansen A. V.: Zh. Prikl. Spektrosk. *6*, 801 (1957).
24. Szczepaniak K., Tramer A.: J. Phys. Chem. *71*, 3055 (1967).
25. Swain C. G., Lupton E. C.: J. Amer. Chem. Soc. *90*, 4328 (1968).
26. Charton M.: Progr. Phys. Org. Chem. *8*, 235 (1971).
27. MacPhee J. A., Panaye A., Dubois J. E.: Tetrahedron *34*, 3553 (1978).
28. Fujita T., Nishioka T.: Progr. Phys. Org. Chem. *12*, 49 (1976).
29. Charton M.: J. Amer. Chem. Soc. *97*, 1552 (1975).
30. Berg V., Gallo R., Klatte G., Metzger J.: J. Chem. Soc. Perkin Trans. 1, *1980*, 1350.

Translated by the author (J. V.).