Russian Chemical Bulletin, International Edition, Vol. 50, No. 9, pp. 1605—1611, September, 2001

Structure and spectra of 1,3,2-dioxaphospholenes

1. Microwave spectra of 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholene and its isotopomers in the ground and excited vibrational states

R. V. Galeev,[a] L. N. Gunderova,[a] A. H. Mamleev,[a]★ A. A. Shapkin,[a] N. M. Pozdeev,[a] O. E. Grikina,[b] M. V. Proskurnina,[b] and L. S. Khaikin[b]★

[a]*Institute of Physics of Molecules and Crystals, Ufa Research Center of the Russian Academy of Sciences,*
151 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 3538
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846

The microwave spectrum of 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholene (**1**) was studied in the frequency range from 7 to 53 GHz. Rotational transitions of the parent molecule in the ground and eleven excited vibrational states and those of its mono-substituted ^{37}Cl, ^{13}C$_{\mathrm{Me}}$, and ^{13}C$_{\mathrm{Cycle}}$ isotopomers in the ground vibrational state were identified. Rotational constants and partial r_s-structure were obtained. The quartic centrifugal distortion constants, dipole moment components $\mu_a = 3.8$D and $\mu_c = 0.24$D (the total dipole moment μ is 3.81D), and the ^{35}Cl quadrupole coupling constants were determined for the parent molecule. The fine structure of the microwave transitions in the parent molecule was analyzed under the assumption of noninteracting methyl groups. The height of the barrier to internal rotation ($V_{30} = V_{03} = 665$ cm^{-1}) and the frequency of torsional vibrations ($\nu = 167$ cm^{-1}) were found. The frequencies of two lowest vibrational modes corresponding to deformation vibrations of the five-membered ring were estimated (ν~100 cm^{-1}) from the relative intensities of rotational transitions for different vibrational states.

Key words: 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholene; microwave spectrum; rotational constants, dipole moment, vibrational frequencies, quadrupole coupling, internal rotation.

1,3,2-Dioxaphospholene derivatives belong to a recently found and poorly studied class of compounds with five-membered phosphorus-containing heterocycles.[1] Studies of their chemical properties revealed enhanced electrophilicity of the 1,3,2-dioxaphospholene system compared to both acyclic phosphorus derivatives and compounds with saturated phosphorus-containing five-membered rings.[2] Based on the results of dipole moment measurements carried out in solution for a number of 2-halo-substituted derivatives of 1,3,2-dioxaphospholene, it was found[3] that the five-membered ring adopts a nonplanar "envelope" conformation and the P—Hal bond has an axial orientation. Studies of the equilibrium structure and spectra of 1,3,2-dioxaphospholenes are of considerable interest.[4] Since experimental solution of such problems faces great difficulties,[5—9] joint use of various experimental methods and quantum-chemical calculations was chosen as the most efficient way of attacking the problem. General formulation of the problem to be solved was discussed earlier.[4] The results of particular quantum-chemical,[4,10—13] gas-phase electron diffraction,[4,13—16] vibrational,[13,17] and microwave[4,18—24] studies have been discussed only briefly or at on-topic conferences.

In this work, we generalize the results obtained in studies of (i) the microwave spectrum of the parent molecule, 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholene (**1**), in the ground and eleven excited vibrational states and (ii) the spectra of its mono-substituted ^{37}Cl, ^{13}C$_{\mathrm{Me}}$, and ^{13}C$_{\mathrm{Cycle}}$ isotopomers in the ground vibrational state. We also report their rotational constants and some other spectral characteristics. The fine structure (FS) of microwave transitions was analyzed under the assumption of noninteracting Me groups. This allowed determination of the height of the barrier to internal rotation and the frequency of torsional vibrations, which was not experimentally detected in the vibrational spectra of molecule **1**.[17] The frequencies of two lowest lying vibrational modes corresponding to deformation vibrations of the five-membered ring were estimated from measurements of the relative intensities of vibrational satellites. Mode assignment was performed.

Experimental

Compound **1** (b.p. 34—35 °C (8 Torr); ^{31}P NMR (δ_P): 170) was synthesized following the known procedure.[2] The microwave spectrum was studied in the frequency range from 7 to

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1528—1534, September, 2001.

53 GHz using a home-made spectrometer. The Stark modulation and two types of double resonance techniques (radiofrequency—microwave and microwave—microwave) were used. The temperature of the absorbing cell was kept near −50 °C and the vapor pressure of compound **1** was maintained in the range from 10^{-2} to 10^{-3} Torr. Each portion of the substance fed into the absorbing cell was purified *in vacuo* following a specially developed procedure. All identified frequencies (a total of 16 tables) were reported earlier.[23,24] Table 1 lists the experimental frequencies of microwave transitions with partially resolved HFS for the ground vibrational state of the parent molecule. The inverse spectral problem was solved in the quasi-rigid asymmetric top approximation and internal rotation was studied using specially developed program packages.[25,26]

Results and Discussion

Ground-state vibrational spectrum of 1. Analysis in the quasi-rigid asymmetric top approximation. Previous quantum-chemical calculations[4,11–13] and gas-phase electron diffraction studies[4,13–16] revealed a nonplanar conformation of the five-membered ring and axial orientation of the P—Cl bond in the equilibrium structure of molecule **1** (Fig. 1). Preliminary calculations of the rotational spectrum of this molecule were carried out using the structural parameters obtained by gas-phase electron diffraction.[4] Similarly to other halogen-con-

Table 1. Experimental frequencies of transitions with partially resolved HFS (f_{exp}), splittings of quadrupole doublets (Δ_{exp}), and differences between the experimental and calculated splitting values (δ) for the parent molecule in the ground vibrational state

J^*	K^*_{-1}	K^*_1 ←	J	K_{-1}	K_1	$2F^* \leftarrow 2F$[a]	f_{exp}	Δ_{exp}	δ
5	0	5	4	0	4	13—11\ 7—5/	10642.38	1.34	−0.06
						11—9\ 9—7/	10643.72		
5	2	4	4	2	3	13—11\ 7—5/	10868.96	0.68	0.04
						11—9\ 9—7/	10869.64		
6	0	6	5	0	5	15—13\ 9—7/	12675.74	1.13	0.02
						13—11\ 11—9/	12676.87		
6	1	5	5	1	4	15—13\ 9—7/	13379.07	0.77	0.03
						13—11\ 11—9/	13379.84		
6	2	5	5	2	4	15—13\ 9—7/	13016.19	0.53	−0.04
						13—11\ 11—9/	13016.72		
7	1	6	6	1	5	17—15\ 11—9/	15527.03	0.86	[b]
						15—13\ 13—11/	15527.89		
7	0	7	6	0	6	17—15\ 11—9/	14696.27	0.85	0.07
						15—13\ 13—11/	14697.12		
7	2	6	6	2	5	17—15\ 11—9/	15149.64	0.50	0.06
						15—13\ 13—11/	15150.14		
9	8	1	8	8	0	21—19\ 15—13/	19674.36	0.99	0.05
						19—17\ 17—15/	19675.35		
11	9	2	10	9	1	25—23\ 19—17/	24052.56	0.76	0.06
						23—21\ 21—19/	24053.32		
12	10	2	11	10	1	27—25\ 21—19/	26237.57	0.76	0.08
						25—23\ 23—21/	26238.33		
29	5	25	29	3	26	61—61\ 55—55/	18391.45	2.39	−0.10
						59—59\ 57—57/	18389.06		
29	4	25	29	4	26	61—61\ 55—55/	18276.19	2.44	−0.01
						59—59\ 57—57/	18273.75		
45	7	38	45	7	39	93—93\ 87—87/	26659.56	1.73	[b]
						91—91\ 89—89/	26657.83		
49	8	41	49	8	42	101—101\ 95—95/	28175.24	1.65	[b]
						99—99\ 97—97/	28173.59		
49	9	41	49	7	42	101—101\ 95—95/	28256.74	1.50	[b]
						99—99\ 97—97/	28255.24		
13	2	11	13	2	12	27—27\ 25—25/	7245.98	5.50	[b]
						29—29\ 23—23/	7251.48		
14	5	10	14	4	10	29—29\ 27—27/	8328.34	2.62	[b]
						31—31\ 25—25/	8325.72		
15	5	11	15	4	11	31—31\ 29—29/	7709.84	4.19	[b]
						33—33\ 27—27/	7705.65		
16	3	13	16	3	14	33—33\ 31—31/	7145.60	5.36	[b]
						35—35\ 29—29/	7150.96		

Note. All values are given in MHz.

[a] Changes in the total angular momentum of the molecule (including nuclear spins).

[b] This transition was not included in the solution of the inverse problem of determination of the quadrupole coupling constants.

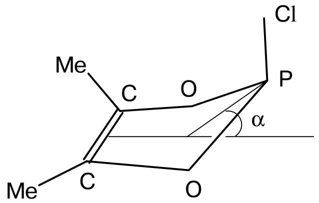

Fig. 1. Overall view of the 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholene molecule.

taining analogs studied earlier in solution,[3] molecule **1** is a slightly asymmetric, prolate top (the asymmetry parameter $k \approx -0.75$). Rotational transitions corresponding to the dipole moment components μ_a and μ_c are allowed. For each value of the quantum number J, transitions of the type ${}^aR_{0,1}$ are grouped together to form rather narrow bands composed of a large number of spectral lines. Identification of the spectrum is complicated by numerous vibrational satellites, the FS of rotational transitions due to the interaction between the internal rotation of two Me groups and the rotation of the entire molecule, and the HFS of rotational transitions due to the nonzero quadrupole moment of chlorine atomic nuclei. No transitions associated with the dipole moment component μ_c were detected in the experiments with the Stark modulation due to the low intensities of corresponding spectral lines. However, weak ${}^cQ$-transitions used for pumping were detected in microwave—microwave double resonance studies using intense ${}^aR$-transitions as reference signals. The observation of the ${}^cQ$-transitions using double resonance technique considerably extended the possibilities of identification of rotational transitions from common coupled energy levels. Extremely high selectivity of double resonance technique allowed weak spectral lines of the ^{13}C isotopomer in natural abundance to be detected and identified.

Forty-six transitions with $3 \le J \le 21$ were identified in the spectrum of the parent molecule. The corresponding spectral lines did not exhibit resolved FS and HFS and were observed as singlets. Twenty-eight transitions with $4 \le J \le 53$ exhibited partially resolved FS and HFS. In this case, the inverse spectral problem was solved using hypothetical frequencies which were thought to be unperturbed by both quadrupole interaction and the interaction with internal rotation. Transitions with partially resolved HFS were observed as doublets (see Table 1) and the hypothetical frequencies were approximately equal to the average experimental frequencies of the doublet components. Transitions with large J values (up to 53) exhibited partially resolved FS components corresponding to the AA and AE ground-state sublevels of torsional vibrations of Me groups. Here, the energy sublevels are denoted following the notations of symmetry types for individual C_3 tops. The experimental frequencies for the AA sublevel were used as hypothetical frequencies. As to the spectra of isotopomers, all the identified transitions with $10 \le J \le 22$ were observed as singlet lines.

The inverse spectral problem was solved in the quartic centrifugal distortion approximation using Watson's Hamiltonian[27]

$$\hat{H}_R = A\hat{P}_z^2 + B\hat{P}_x^2 + C\hat{P}_y^2 - \Delta_J\hat{P}^4 - \Delta_{JK}\hat{P}^2\hat{P}_z^2 - \Delta_K\hat{P}_z^4 - 2\delta_J\hat{P}^2\left(\hat{P}_x^2 - \hat{P}_y^2\right) - \delta_K\left[\hat{P}_z^2\left(\hat{P}_x^2 - \hat{P}_y^2\right) + \left(\hat{P}_x^2 - \hat{P}_y^2\right)\hat{P}_z^2\right] . \quad (1)$$

The rotational constants A, B, and C determined from experimental data for seventy-four transitions in the parent molecule[23] are listed in Table 2. The quartic centrifugal distortion constants (in kHz) are as follows: $\Delta_J = 0.2152(25)$, $\Delta_{JK} = -0.657(24)$, $\Delta_K = 1.10(51)$, $\delta_J = -0.00513(99)$, and $\delta_K = -0.123(20)$. Rotational constants of isotopomers were calculated assuming that their quartic centrifugal distortion constants are equal to those of the parent molecule. The values of rotational constants found in this work (see Table 2) are in good

Table 2. Rotational constants (A—C/MHz) and principal moments of inertial (I/amu Å^2, with a transformation coefficient of 505379.1) for the parent molecule and mono-substituted ^{37}Cl, ^{13}C$_{\text{Me}}$, and ^{13}C$_{\text{cycl}}$ isotopomers in the ground vibrational state

Parameter	Isotopomer			
	Parent molecule	^{37}Cl	^{13}C$_{\text{Me}}$	^{13}C$_{\text{cycl}}$
A	2187.556(17)	2171.929(113)	2159.995(101)	2182.999(103)
B	1163.818(2)	1139.505(3)	1150.514(4)	1159.864(4)
C	1016.607(2)	1001.310(2)	1001.563(4)	1012.744(3)
I_A	231.02453(180)	232.68675(1210)	233.97235(1090)	231.50679(1090)
I_B	434.24238(70)	443.50758(120)	439.26376(150)	435.72272(140)
I_C	497.12337(100)	504.71792(100)	504.59043(200)	499.01959(170)
N*	74	30	24	38
σ**	0.11	0.08	0.13	0.13

Note. The standard deviations are given in parentheses.

* The number of experimental frequencies of rotational transitions.

** The standard deviation of calculated frequencies from experimental values (in MHz).

agreement with previous inferences about nonplanar ring conformation and axial orientation of the P—Cl bond in molecule **1**.[14] Joint analysis of the gas-phase electron diffraction and microwave spectroscopy data allowed the equilibrium structure to be determined more correctly. The deviation angle of the P atom from the plane passing through the other four atoms of the five-membered ring, φ, was estimated at 18.7±0.8°.[15,16] Based on the experimental values of rotational constants, we calculated the principal moments of inertia and the following parameters of partial r_s-structure (in Å) for molecule **1**

C=C	1.347(9)	Cl...C$_{cycl}$	3.317(4)	C$_{cycl}$...C$_{Me}$	2.549(5)
C—C$_{Me}$	1.423(5)	Cl...C$_{Me}$	4.470(2)	C$_{Me}$...C$_{Me}$	3.321(4)

The dipole moment components, $\mu_a = 3.8(2)$ D and $\mu_c = 0.24(2)$ D, were determined from measurements of the Stark effect in the rotational spectrum of the parent molecule; the total dipole moment, μ, is 3.81(20) D.

Quadrupole interaction. Initially, the hyperfine splitting due to the quadrupole moment of ^{35}Cl nucleus was observed for the $^cQ_{1,0}$-transitions $14_{5,10}$←$14_{4,10}$ (8327 MHz) and $15_{5,11}$←$15_{4,11}$ (7708 MHz) in the spectrum of the parent molecule recorded using microwave—microwave double resonance technique (see Table 1). These transitions were used for pumping and observed as doublets with splittings of 2.6 and 4.2 MHz, respectively. This allowed us to obtain preliminary estimates of the quadrupole coupling constants and to perform targeted search for μ_a-transitions with partially resolved HFS (doublets with detectable splitting). The quadrupole coupling constants were determined from the frequencies of twelve doublets corresponding to the μ_a-transitions with $3 \le J \le 29$ by the least squares method at the first-order level of theory of quadrupole interaction. Corrections to rotational energy levels were calculated by the formula[28]

$$E_Q(J,F) = \\ = 2\left[\chi_{aa}\left(\frac{\partial E}{\partial A}-\frac{\partial E}{\partial B}\right)+\chi_{cc}\left(\frac{\partial E}{\partial C}-\frac{\partial E}{\partial B}\right)\right]\frac{f(I,J,F)}{J(J+1)}, \quad (2)$$

where $f(I, J, F)$ is the Casimir function and χ_{aa} and χ_{cc} are the components of the quadrupole coupling tensor in the system of principal axes of inertia of the molecule. Minimization was performed with fixed values of rotational and centrifugal distortion constants. The parameters χ_{aa}, χ_{cc}, and $\chi_{bb} = -(\chi_{aa} + \chi_{cc})$ were found to be 8.99(34), −27.49(41), and 18.50 MHz, respectively.

Internal rotation of Me groups. Previously,[29] it was shown that four sublevels, AA, AE, (EE)$_+$, and (EE)$_-$ (denoted following the notations of symmetry types for individual C_3 tops), with a ratio of statistical weights of 16 : 32 : 8 : 8 correspond to the ground state of torsional vibrations of two equivalent Me groups ($v = v' = 0$) in molecules with C_s symmetry. Therefore, one could expect a complex pattern for the FS of spectral lines of compound **1** due to the interaction between internal rotation of Me groups and the rotation of the entire molecule. However, initially identified transitions with small quantum numbers J exhibited no resolved FS. This was an indication of a rather high potential barrier which hinders internal rotation. A more thorough search for the FS of rotational transitions was undertaken after preliminary calculations with different barrier heights.

Using radiofrequency—microwave double resonance techniques, we detected resolved components of a FS of spectral lines of ^aQ-transitions with large quantum numbers J and K_1 ($48 \le J \le 53$, $41 \le K_1 \le 46$) and small asymmetry splitting parameter in the spectrum of the parent molecule and measured their frequencies. These components correspond to torsional states with the largest statistical weights (AA and AE). Weak radiofrequency $^cQ_{1,0}$-transitions $48_{8,41}$←$48_{7,41}$ (12.0 MHz), $50_{8,43}$←$50_{7,43}$ (4.3 MHz), $51_{9,43}$←$51_{8,43}$ (29.9 MHz), $52_{9,44}$←$52_{8,44}$ (17.7 MHz), and $53_{9,45}$←$53_{8,45}$ (10.8 MHz) were used for pumping. In addition to conventional allowed ^aQ-transitions, for the state AE we also observed forbidden transitions that are due to strong mixing of rotational wave functions through the perturbation term $\delta_K = F\gamma w_{00}{}^{(+1)} \langle J_{K_{-1},K}|P_c|J_{K_{-1}+1,K}\rangle$ relating two close-lying energy levels, $J_{K_{-1},K}$ and $J_{K_{-1}+1,K}$, to each other. The appearance of forbidden transitions was accompanied by a decrease in the intensities of the allowed transitions. Information on the height of the barrier to internal rotation, obtained after interpretation of the FS of spectral lines of ^aQ-transitions with large quantum numbers J allowed us to find yet another type of transitions with partially resolved FS (^aR-transitions between energy levels with $12 \le J \le 20$ and $6 \le K_{-1} \le 8$).

To describe the spectrum in the torsional state belonging to the symmetry type AE, we used the effective rotational Hamiltonian for a molecule with two equivalent internal symmetric tops

$$\hat{H}_{vv} = \hat{H}_R + F\Sigma_n(w_{vv}^{(+n)}\hat{P}_+^n + w_{vv}^{(-n)}\hat{P}_-^n), \quad (3)$$

where

$$\hat{P}_+ = \alpha\hat{P}_a + \gamma\hat{P}_c, \qquad \hat{P}_- = \beta\hat{P}_b,$$
$$\alpha = (\lambda_a I_\alpha)/I_A, \qquad \beta = (\lambda_b I_\alpha)/I_B, \qquad \gamma = (\lambda_c I_\alpha)/I_C.$$

This expression has the same form as the effective rotational Hamiltonian for a molecule with one symmetric top (expression (3) is written using the same notations as those used in Ref. 28). The perturbation coefficients $w_{vv}{}^{(\pm n)}$ can be expressed as linear combinations of tabulated[28] perturbation coefficients $W_{v\sigma}{}^{(n)}$ for the case of single internal symmetric top. For the state AE, the inverse spectral problem was solved using the experimental frequencies of 23 transitions with $J \le 53$. The experimental frequencies of transitions with $J \ge 48$ (here, both the AA—AE and hyperfine splitting are observed) were corrected for quadrupole interaction. In addition to rotational constants, we also determined two effective parameters $F\alpha w_{00}{}^{(+1)}$ and $F\gamma w_{00}{}^{(+1)}$ (−0.204(11) and −0.05542(46) MHz, respectively), which describe the interaction between internal rotation and rotation of the entire molecule at the first-order level of perturbation theory. Centrifugal distortion constants were fixed and assumed to be equal to those of the torsional state belonging to the symmetry type AA. It was found that rotational constants for the states AE and AA coincide within the limits of standard deviations. The standard deviation of the calculated frequencies from experimental ones was found to be 0.06 MHz.

We considered the potential function of internal rotation for two noncoupled internal tops

$$V(\alpha_1,\alpha_2) = 0.5V_{30}(1 - \cos3\alpha_1) + 0.5V_{03}(1 - \cos3\alpha_2). \quad (4)$$

In this approximation, the above-mentioned values of the effective parameters $F\alpha w_{00}{}^{(+1)}$ and $F\gamma w_{00}{}^{(+1)}$ calculated for the parent molecule with the structural parameters $F = 162$ GHz, $\alpha = 0.0092$, $\gamma = 0.0025$, and $I_\alpha = 3.15$ amu Å^2 correspond to a potential barrier height ($V_{30} = V_{03}$) of 665 cm^{-1} and a frequency of torsional vibrations of 167 cm^{-1}.

Microwave spectrum of the parent molecule in excited vibrational states. We found that each spectral line originated from a rotational transition of the molecule in the ground vibrational state has observable vibrational satellites, *i.e.*, spectral lines corresponding to rotational transitions between excited vibrational states of the molecule. Analysis of the intensity distribution and spectral pattern allowed us to select the vibrational satellites corresponding to two lowest-lying vibrational modes n_1 and n_2.[23,24] The values of rotational constants determined in the quasi-rigid asymmetric top approximation from the experimental frequencies of transitions for excited vibrational states of the parent molecule are listed in Table 3. They were calculated assuming that the centrifugal distortion constants are equal to those of the ground vibrational state. Based on the measurements of the relative intensities of rotational transitions, we estimated the frequencies of two lowest vibrational modes (ν ~ 100 cm^{-1}) and found that they coincide within the limits of experimental error.

Appreciable difference between the pattern of the rotational spectrum for the vibrational state (0,3) and the spectral pattern of the quasi-rigid asymmetric top should also be pointed out (see Table 3). Here, the standard deviation, σ, of calculated frequencies from experimental values, which is usually comparable with the experimental error (0.05 MHz), equals 2.13 MHz and far exceeds the σ values for other vibrational states.

Comparison of experimental vibrational frequencies of parent molecule obtained by microwave spectroscopy with results of quantum-chemical calculations. Restricted Hartree—Fock calculations[4,11—13] predict four vibrational modes corresponding to ring puckering (ν = 98 cm^{-1}) and twisting (ν = 138 cm^{-1}) and to torsional vibrations of Me groups (ν = 175 and 188 cm^{-1}) in the frequency range below 200 cm^{-1}.

Since the experimental frequencies of torsional vibrations (ν = 167 cm^{-1}) were found from analysis of the FS of microwave transitions in the parent molecule performed assuming noninteracting Me groups, the splitting of the energy sublevels in the upper torsional state ($v = 1$) is negligible (Fig. 2). A more thorough analysis requires the use of a potential function with inclusion of correction for the interactions between torsional vibrations of Me groups. Such a potential function can be expressed as follows

$$V(\alpha_1,\alpha_2) = 0.5V_{30}(1 - \cos3\alpha_1) + \\ + 0.5V_{03}(1 - \cos3\alpha_2) + V'_{12}\sin3\alpha_1\sin3\alpha_2. \quad (5)$$

The largest experimental value of the parameter V'_{12}, determining the interaction between two equivalent Me groups reaches 4.8% of the height of the potential barrier, V_{30}.[30,31] Using this ratio, one gets that the splitting of energy sublevels in the state $v = 1$ increases to 13.1 cm^{-1} (see Fig. 2, *b*). The average frequency of

Table 3. Rotational constants (*A*, *B*, *C*/MHz) for the parent molecule in the ground and excited states of two lowest vibrational modes (n_1 and n_2)

n_1,n_2	*A*	*B*	*C*	*N**	σ**
0,0	2187.556(17)	1163.818(2)	1016.607(2)	74	0.11
1,0	2187.30(32)	1164.2667(99)	1017.3801(79)	22	0.13
2,0	2187.35(36)	1164.727(11)	1018.1384(85)	16	0.12
3,0	2188.50(24)	1165.2128(70)	1018.8771(55)	12	0.07
4,0	2180.8(22)	1165.41(7)	1019.81(5)	6	0.27
0,1	2190.69(27)	1163.0632(88)	1015.8414(74)	23	0.14
0,2	2193.52(37)	1162.325(12)	1015.110(9)	19	0.15
0,3	2202.037(6100)	1162.08(18)	1014.10(15)	15	2.13
0,4	2182.85(39)	1163.604(56)	1011.788(10)	6	0.04
1,1	2193.91(42)	1163.660(14)	1016.386(12)	14	0.14
1,2	2197.87(306)	1162.95(13)	1015.59(17)	13	0.25
2,1	2183.71(93)	1163.649(29)	1017.704(24)	9	0.28

Note. The standard deviations are given in parentheses.

* The number of experimental frequencies of rotational transitions.

** The standard deviation of calculated frequencies from experimental values (in MHz).

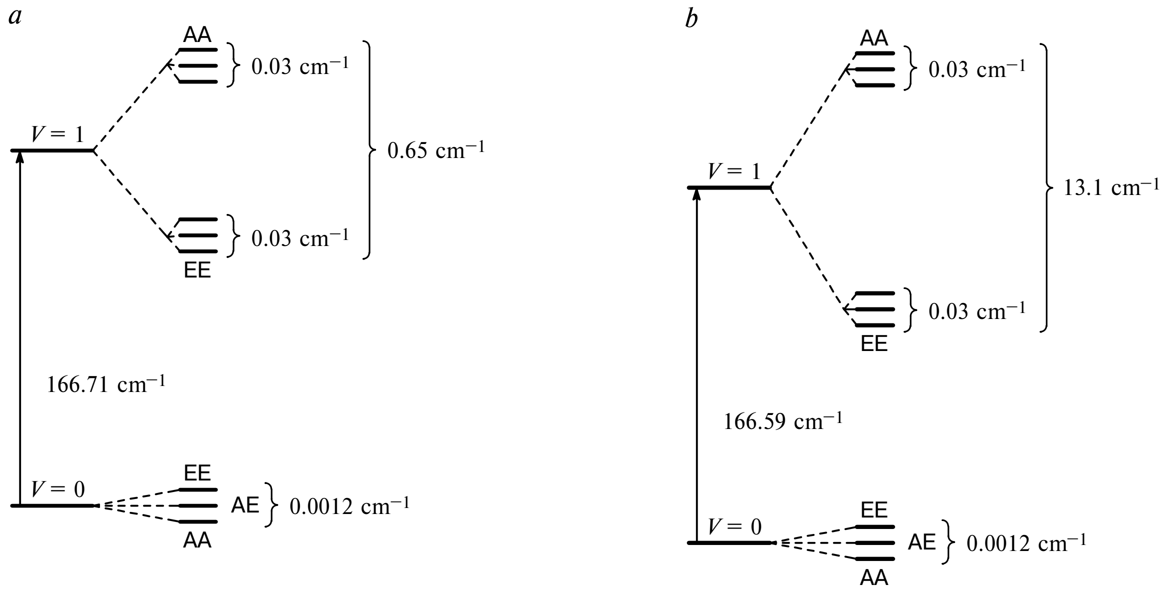

Fig. 2. Scheme of energy sublevels for torsional vibrations of two Me groups in the parent molecule in the ground (v = 0) and first excited (v = 1) states constructed assuming noncoupled internal tops (*a*) and corrected for the top—top coupling (see expression (5)) (*b*). The coupling constant V'_{12} = −31.9 cm^{-1} was taken to be 4.8% of the experimental height of the potential barrier V_{30}.

the doublet remains virtually unchanged. Hence it can be used for the determination of the scale factor when comparing the experimental frequencies of torsional vibrations with the results of quantum-chemical calculations. A scale factor value of 0.92 found in this work corresponds to a doublet splitting of 12 cm^{-1} (ν = 161 and 173 cm^{-1}). The magnitude of the coupling constant, V'_{12}, is −29.3 cm^{-1} or 4.4% of the experimental barrier height value (V_{03} = V_{30} = 665 cm^{-1}). Thus, the results of quantum-chemical calculations[4,11–13] for torsional vibrations of Me groups are in good agreement with the microwave spectroscopy data.

The existence of two lowest vibrational modes, n_1 and n_2, with frequencies ν ~ 100 cm^{-1} and their assignment is also consistent with the results of quantum-chemical calculations.[4,11–13] All vibrational satellites observed in the microwave spectrum of the parent molecule belong to different excited states of these modes and can be assigned using the data listed in Table 4. Since the ground state of molecule **1** is characterized by a nonplanar ring conformation, excitation of a ring puckering vibration leads to flattening of the five-membered ring and to a decrease in the inertial defect Δ_C. Excitation of a twisting vibration of the ring should not lead to a decrease in Δ_C. Therefore, analysis of the character of changes in Δ_C upon excitation of vibrations (see Table 4) allows the modes n_1 and n_2 to be assigned to twisting and puckering vibrations of the five-membered ring, respectively.

There is yet another argument in favor of this assignment. As mentioned above, the pattern of the rotational spectrum for the vibrational state (0,3) differs appreciably from the spectral pattern of the quasi-rigid asymmetric top (see Table 3). We believe that the observed deviation is due to strong rotation-vibration interaction, which can occur in the case of intramolecular motion associated with ring inversion. Analysis of vibrational spectra performed with scaling of quantum-chemical force field showed that in the case of molecule **1** this can only be a complex two-dimensional motion which includes both ring puckering vibration and wagging vibration of the P—Cl bond.[17] It was found that such a

Table 4. Inertial defects (Δ/amu Å^2) in the ground and excited vibrational states of two lowest vibrational modes (n_1 and n_2) and changes in the inertial defects (δΔ) upon excitation of the vibrational modes to upper levels for the parent molecule

n_1,n_2	Δ/amu Å^2			δΔ/amu Å^2		
	$\Delta_A = I_B + I_C - I_A$	$\Delta_B = I_C + I_A - I_B$	$\Delta_C = I_A + I_B - I_C$	$\delta\Delta_A = 2\Sigma m_i \delta a_i^2$	$\delta\Delta_B = 2\Sigma m_i \delta b_i^2$	$\delta\Delta_C = 2\Sigma m_i \delta c_i^2$
0,0	700.3413	293.9055	168.1435			
0,1	701.3282	293.6678	167.7202	0.9869	−0.2377	−0.4233
0,2	702.2602	293.4518	167.3402	1.9189	−0.4537	−0.8033
1,0	699.7691	293.7221	168.3809	−0.5722	−0.18342	0.2374
2,0	699.23314	293.51814	168.57386	−1.10816	−0.38736	0.43036

motion studied taking 3-phospholene molecule as an example[9] is described by a potential surface with two equivalent wells. In the high barrier approximation, vibrational energy levels are degenerate. However, if the barrier between the wells is sufficiently low, these levels become split. The splitting value becomes comparable with the rotational energy and a strong, resonance-type, rotation-vibration Coriolis interaction occurs, which is responsible for anomalies in the rotational spectrum of the molecule.

References

1. I. F. Lutsenko, M. V. Proskurnina, T. N. Kudryavtseva, N. B. Karlstedt, and T. G. Shestakova, *Zh. Obshch. Khim.*, 1981, **51**, 961 [*J. Gen. Chem. USSR*, 1981, **51** (Engl. Transl.)].
2. N. B. Karlstedt, T. N. Kudryavtseva, M. V. Proskurnina, and I. F. Lutsenko, *Zh. Obshch. Khim.*, 1982, **52**, 1974 [*J. Gen. Chem. USSR*, 1982, **52** (Engl. Transl.)].
3. E. A. Ishmaeva, I. I. Patsanovskii, M. V. Proskurnina, E. N. Strelkova, N. B. Karlstedt, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, 1983, **272**, 136 [*Dokl. Chem.*, 1983 (Engl. Transl.)].
4. R. V. Galeev, L. N. Gunderova, G. R. Garipova, A. H. Mamleev, N. M. Pozdeev, L. S. Khaikin, M. V. Proskurnina, L. V. Vilkov, N. S. Zefirov, M. Alcolea Palafox, and J. E. Boggs, *Tr. V Vsesoyuznogo soveshchaniya po izucheniyu struktury molekul v gazovoi faze* [*Proc. Vth All-Union Meeting on Studies of the Molecular Structure in the Gas Phase*], *Mezhvuzovskii sb.*, IKhTI, Ivanovo, 1990, 107 (in Russian).
5. A. C. Legon, *Chem. Rev.*, 1980, **80**, 231.
6. K. Tamagawa and R. L. Hilderbrandt, *J. Am. Chem. Soc.*, 1984, **106**, 20.
7. L. W. Richardson, P. W. Jagodzinski, M. A. Harthcock, and J. Laane, *J. Chem. Phys.*, 1980, **73**, 5556.
8. J. R. Durig, B. J. Streusand, Y. S. Li, L. Richardson, and J. Laane, *J. Chem. Phys.*, 1980, **73**, 5564.
9. M. A. Harthcock and J. Laane, *J. Chem. Phys.*, 1983, **79**, 2103.
10. M. Alcolea Palafox, V. I. Perevozchikov, J. E. Boggs, and L. S. Khaikin, *J. Mol. Struct. THEOCHEM.*, 1991, **228**, 315.
11. L. S. Khaikin, E. A. Zhilinskaya, O. E. Grikina, and L. V. Vilkov, *16th Austin Symp. on Molecular Structure, Austin, Texas USA, March 4—6*, Austin, 1996, S7, p. 110.
12. L. S. Khaikin, O. E. Grikina, E. A. Zhilinskaya, and B. I. Zhilinskii, *18th Austin Symp. on Molecular Structure*, *Austin, Texas USA*, *March 6—8*, Austin, 2000, S19, p. 91.
13. O. E. Grikina, L. S. Khaikin, and M. Alcolea Palafox, in *Spectroscopy of Biological Molecules: Modern Trends*, Eds. P. Carmona, R. Navarro, and A. Hernanz, Kluver Academic Publishers, Dordrecht—Boston—London, 1997, 539.
14. L. S. Khaikin, V. V. Smirnov, M. V. Proskurnina, A. V. Golubinskii, L. V. Vilkov, and N. S. Zefirov, *Dokl. Akad. Nauk SSSR*, 1987, **296**, 169 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
15. L. S. Khaikin, V. A. Sipachev, A. V. Beklemishev, N. M. Pozdeev, E. A. Zhilinskaya, M. V. Proskurnina, and L. V. Vilkov, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1997, **38**, 222 [*Moscow Univ. Bull., Ser. 2, Chem.*, 1997, **38** (Engl. Transl.)].
16. L. S. Khaikin, V. A. Sipachev, A. V. Beklemishev, M. V. Proskurnina, N. M. Pozdeev, and L. V. Vilkov, *16th Austin Symp. on Molecular Structure, Austin, Texas USA, March 4—6*, Austin, 1996, S8, p. 111.
17. A. Kh. Plyamovatyi, S. A. Katsuba, M. V. Proskurnina, L. S. Khaikin, O. E. Grikina, M. Alcolea Palafox, R. R. Shagidullin, and J. E. Boggs, *16th Austin Symp. on Molecular Structure, Austin, Texas USA, March 4—6*, Austin, 1996, SN24, p. 145.
18. R. V. Galeev, L. N. Gunderova, G. R. Garipova, A. H. Mamleev, N. M. Pozdeev, O. L. Varand, M. V. Proskurnina, and L. S. Khaikin, *13th Austin Symp. on Molecular Structure, Austin, Texas USA, March 12—14*, Austin, 1990, S17, p. 103.
19. R. V. Galeev, L. N. Gunderova, G. R. Garipova, A. H. Mamleev, N. M. Pozdeev, M. V. Proskurnina, and L. S. Khaikin, *14th Austin Symp. on Molecular Structure*, *Austin, Texas USA, March 2—4*, Austin, 1992, S18, p. 101.
20. R. V. Galeev, L. N. Gunderova, A. H. Mamleev, and N. M. Pozdeev, *Xth All-Union Symposium and School on High Resolution Molecular Spectroscopy*, *Proc. SPIE*, 1992, **1811,** 228.
21. R. V. Galeev, L. N. Gunderova, G. R. Garipova, A. H. Mamleev, N. M. Pozdeev, O. L. Varand, M. V. Proskurnina, and L. S. Khaikin, *Xth All-Union Symposium and School on High Resolution Molecular Spectroscopy*, *Proc. SPIE*, 1992, **1811**, 235.
22. R. V. Galeev, L. N. Gunderova, G. R. Garipova, A. H. Mamleev, N. M. Pozdeev, M. V. Proskurnina, and L. S. Khaikin, *16th Austin Symp. on Molecular Structure, Austin, Texas USA, March 4—6*, Austin, 1996, SN16, p. 137.
23. R. V. Galeev, A. H. Mamleev, L. N. Gunderova, and N. M. Pozdeev, *Mikrovolnovyi spektr 4,5-dimetil-2-khlor-1,3,2-dioksafosfolena osnovnogo izotopnogo sostava i monozameshchennykh molekul s izotopami* ^{37}Cl, $^{13}C_{Me}$, $^{13}C_{cycl}$ [*Microwave Spectrum of 2-Cl-4,5-dimethyl-1,3,2-dioxaphospholene and Mono-Substituted Molecules with* ^{37}Cl, $^{13}C_{Me}$, *and* $^{13}C_{cycl}$], Deposited in and available from VINITI, No. 1739-B94, Moscow, 1994, 35 pp. (in Russian).
24. R. V. Galeev, L. N. Gunderova, A. H. Mamleev, and N. M. Pozdeev, A. A. Shapkin, and L. S. Khaikin, *Elektronnyi zhurnal "Issledovano v Rossii"* [*Electronic journal "Investigated in Russia"*], 2001, **18**, 188 (in Russian). This material can be accessed *via* the Internet at URL http://zhurnal.ape.relarn.ru/articles/2001/018.pdf.
25. L. N. Gunderova and N. M. Pozdeev, *Kvazizhestkii asimmetrichnyi volchok. Kompleks programm* [*A Program Package for Quasi-Rigid Asymmetric Top*], Deposited in and available from VINITI, No. 2135-B89, Moscow, 1989, 39 pp. (in Russian).
26. L. N. Gunderova and N. M. Pozdeev, *Kompleks programm dlya issledovaniya mikrovolnovykh spektrov molekul s vnutrennim vrashcheniem* [*A Program Package for Interpreting Microwave Spectra of Molecules with Internal Rotation*], Deposited in and available from VINITI, No. 254-B92, Moscow, 1992, 46 pp. (in Russian).
27. J. K. G. Watson, *J. Chem. Phys.*, 1967, **46**, 1935.
28. J. E. Wallrab, *Rotational Spectra and Molecular Structure*, Academic Press, New York—London, 1967.
29. M. L. Sage, *J. Chem. Phys.*, 1961, **35**, 142.
30. A. Trinkaus, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, 1973, **28A**, 750.
31. G. K. Pandey, H. Luntz, and H. Dreizler, *Z. Naturforsch.*, 1976, **31A**, 1413.

Received January 4, 2001;
in revised form May 14, 2001