High Resolution Microwave Spectra of Pyridine-N-oxide and α-Picoline-N-oxide

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The rotational spectra of pyridine-N-oxide and α-picoline-N-oxide (= 2-methylpyridine-N-oxide) have been observed by means of pulsed microwave spectroscopy. For both molecules, the ^{14}N quadrupole coupling constants have been obtained. For α-picoline-N-oxide, in addition the parameters of the internal rotation motion and the centrifugal distortion constants have been determined.

Introduction

The microwave spectrum of pyridine-N-oxide has been extensively studied by Sørensen and coworkers [1, 2], who have also reported a complete substitution structure for this molecule [2]. However, no hyperfine structure due to quadrupole coupling of the nitrogen nucleus has so far been observed, and the electronic situation around this nucleus is therefore uncertain.

The pure rotational spectrum of α-picoline-N-oxide has only recently been assigned [3]. Again, no hyperfine structure or torsional fine structure arising from internal rotation of the methyl group has been observed.

In an attempt to provide information about the rather uncommon bonding situation in these molecules, we have studied their rotational spectra under the higher resolution obtainable with our travelling wave Fourier transform spectrometers.

Experimental

We used commercially available pyridine-N-oxide (henceforward abbreviated PYROX) and α-picoline-N-oxide (PICOX). Drawings of the two molecules in their respective inertia axes systems are given in Figure 1. PYROX was in our stock for years and had to be crystallized from acetone before use in order to remove water and impurities. Residual solvent was then removed *in vacuo*. Both substances hydratize readily, so that they were stored without access of air. Nevertheless, conditioning of the waveguide sample cells was difficult. Both substances are solid at room temperature, but sublime when moderately heated.

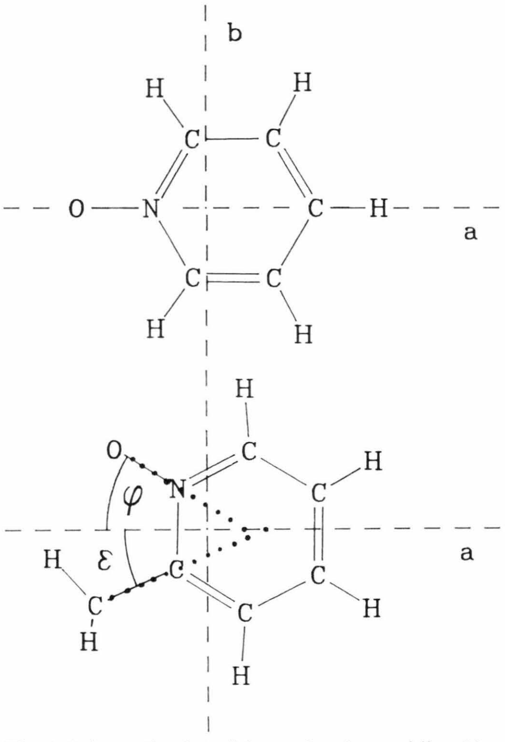

Fig. 1. Schematic plot of the molecules pyridine-N-oxide and α-picoline-N-oxide in their inertia axes systems. φ angle between principal inertia axis and principal axis of coupling tensor (assumed), ε angle between principal inertia axis and internal rotation axis.

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The spectra were recorded at temperatures ranging from room temperature (PICOX) to −30 °C (PYROX), and pressures of 0.1 Pa to 0.3 Pa (0.7–2.2 mTorr). We used our pulsed microwave Fourier transform spectrometers in X-band (8.0–12.4 GHz, PYROX) [4], V-band (26.4–40 GHz, PICOX) [5], and K-band (18–26.4 GHz, both) [6]. In cases where lines were members of close multiplets, whether accidentally or due to nuclear hyperfine or torsional fine structure, the frequencies were taken from least squares fits to the time domain signals [7], rather than from the Fourier transform spectra. An example is presented in Fig. 2. It shows a 4-MHz-section out of the absorption spectrum [8] of α-picoline-N-oxide, where two ^{b}Q-branch transitions accidentally come fairly close, both split by internal rotation.

Analysis

Nuclear hyperfine structures were analyzed using first order perturbation theory (programme HT1NQ [9]). In all cases, we used the hyperfine offsets relative to the centre frequencies, which in turn were adjusted to minimize the sum of the remaining deviations from the calculated patterns. For PYROX, these centre frequencies were compared to calculated frequencies using the data given in [1]. In the case of PICOX, only very few rotational transitions showing nuclear quadrupole hyperfine structure could be observed, because the spectrum was rather weak in general and the

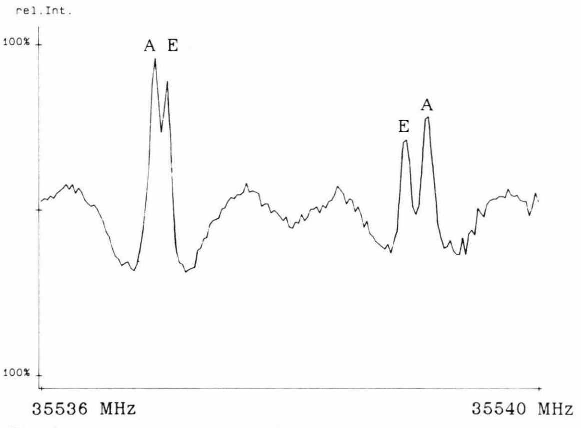

Fig. 2. 4-MHz-section out of the rotational absorption spectrum of α-picoline-N-oxide, showing the transitions J, K_-, $K_+ = 39$, 17, 22–39, 16, 23 (left) and 26, 14, 12–26, 13, 13 (right). Experimental conditions were: room temperature, pressure ∼0.3 Pa = 2 mTorr, acquisition time 20 μs, $8 \cdot 10^6$ cycles, FFT-length 4096 points, delay 1000 ns. Symmetry species of the torsional fine structure components are given.

Table 1. Observed frequencies of resolved hyperfine structure multiplets of pyridine-N-oxide and α-picoline-N-oxide. ν_0 centre frequency, $\Delta\nu$ quadrupole offset, $\delta\nu_0$ deviation of centre frequency from calculated value, $\delta\Delta\nu$ deviation of offset from calculated value (using constants of Table 2).

J'	K'_-	K'_+	J''	K''_-	K''_+	$F'-F''$	ν_0/MHz	$\Delta\nu$/ kHz	$\delta\nu_0$/ kHz	$\delta\Delta\nu$/ kHz
pyridine-N-oxide (PYROX)										
4	3	2	3	3	1		19 048.088		−10	
						5−4		+ 66		+1
						4−3		−201		−1
						3−2		+163		−1
5	2	3	4	2	2		25 435.421		−15	
						6−5/		+ 26		−1
						4−3				
						5−4		− 56		+1
5	3	2	4	3	1		24 244.533		−11	
						6−5		+ 46		+2
						5−4		−119		−1
						4−3		+ 78		−2
5	4	1	4	4	0		23 842.740		− 5	
						6−5		+ 65		+2
						5−4		−180		0
						4−3		+133		−1
6	2	5	6	0	6		20 919.468		−18	
						7−7/		+ 33		0
						5−5				
						6−6		− 63		+1
7	1	6	7	1	7		21 886.229		−15	
						8−8		+ 55		0
						7−7		−134		−1
						6−6		+ 82		0
7	2	5	7	2	6		11 962.174		− 8	
						8−8		+ 63		−1
						7−7		−155		0
						6−6		+ 97		+2
12	4	8	12	4	9		11 528.791		0	
						13−13/		+ 53		−2
						11−11				
						12−12		−108		+1
19	6	13	19	6	14		20 119.649		+ 2	
						20−20/		+ 49		0
						18−18				
						19−19		− 99		−1
α-picoline-N-oxide (PICOX)										
5	3	3	4	2	2		24 803.337		− 1	
						6−5/		− 26		−1
						4−3				
						5−4		+ 48		+1
6	4	3	5	3	2		32 862.929		+10	
						7−6/		+ 20		+2
						5−4				
						6−5		− 41		−1
6	4	2	5	4	1		23 525.099		− 7	
						7−6/		+ 31		+1
						5−4				
						6−5		− 59		−1
6	4	3	5	4	2		23 017.489		+12	
						7−6		− 23		+3
						6−5		+ 52		0
						5−4		− 33		−2

Table 2. ^{14}N quadrupole coupling constants of pyridine-N-oxide (PYROX) and α-picoline-N-oxide (PICOX).

Constant	PYROX	PICOX
$\chi^+ \equiv \chi_{bb} + \chi_{cc}$	$-838\,(3)$ kHz	$-443\,(10)$ kHz
$\chi^- \equiv \chi_{bb} - \chi_{cc}$	$-878\,(3)$ kHz	$-\;36\,(19)$ kHz
γ^{a}	$-\;0.056$	$-\;0.764$
σ^{b}	1.2 kHz	1.7 kHz
$\overline{\Delta\nu}^{c}$	92 kHz	37 kHz
$\chi_{aa} = -\chi^+$	$+838\,(3)^{d}$ kHz	$+443\,(10)^{d}$ kHz
$\chi_{bb} = 1/2\,(\chi^+ + \chi^-)$	$-858\,(2)^{d}$ kHz	$-240\,(7)^{d}$ kHz
$\chi_{cc} = 1/2\,(\chi^+ - \chi^-)$	$+\;20\,(2)^{d}$ kHz	$-203\,(14)^{d}$ kHz
$\chi_{bb} - \chi_{aa} = 1/2\,(3\,\chi^+ + \chi^-)$	$-1696\,(6)^{d}$ kHz	$-683\,(10)^{d}$ kHz
$\chi_{xx} - \chi_{zz} = (\chi_{bb} - \chi_{aa})/\cos 2\,\varphi^{e}$	$-1696\,(6)$ kHz	-1548 kHz^{f}

[a] γ is the correlation coefficient of χ^+ and χ^- (dimensionless).

[b] σ is the standard deviation of the fit.

[c] $\overline{\Delta\nu}$ is the mean experimental splitting.

[d] Errors have been calculated using the relation [18] $\sigma^2(i \pm j) = \sigma^2(i) + \sigma^2(j) \pm 2\gamma \cdot \sigma(i) \cdot \sigma(j)$ (σ^2 = variance; i, j = random variables).

[e] For the meaning of φ, see Fig. 1; χ_{xx} and χ_{zz} are the two in-plane principal elements of the coupling tensor.

[f] φ assumed to be 31.9° from the structure.

quadrupole splittings were barely resolvable. In this case, the centre frequencies were, along with many others (see below), used for the determination of the centrifugal distortion constants. The measured line frequencies are compiled in Table 1. The results of the quadrupole coupling analyses are presented in Table 2. Fit parameters were the linear combinations χ^+ ($\equiv \chi_{bb} + \chi_{cc}$) and χ^- ($\equiv \chi_{bb} - \chi_{cc}$). The uncertainties in the coupling constants χ_{aa}, χ_{bb}, χ_{cc}, and ($\chi_{bb} - \chi_{cc}$) have been calculated using error propagation including the correlation of χ^+ and χ^-.

For the internal rotation analysis (only PICOX), high-J transitions in V-band were recorded. With one exception ($J, K_- = 10{,}8$–$9{,}8$ K-doublet), only Q-branch transitions, with J ranging from 20 to 40, were observed. Using our programme KC3IAM [10], we were able to determine the barrier to internal rotation, V_3, the angle between the internal rotation axis and the a principal inertia axis, ε, and, however with unsatisfac-

Table 3. Observed internal rotation splittings of V-band rotational transitions of α-picoline-N-oxide. ν_0 frequency corrected for internal rotation effect, $\delta\nu_0$ deviation of this frequency from value calculated with centrifugal distortion and rotational constants of Table 6, $\tau = K_- - K_+$, ν_A frequency of component with symmetry species $\Gamma = A$, ν_E dto., but $\Gamma = E$, δ deviation of splitting from calculated value (using final values in Table 4). Asterisks mark frequencies not used for fit.

J'	K'_-	K'_+	τ'	J''	K''_-	K''_+	τ''	ν_0/MHz	ν_A/MHz	$\delta\nu_0$/kHz	$\nu_A - \nu_E$/MHz	δ/kHz
10	8	2	6	9	8	1	7	38 266.859*	38 266.852	−151*	0.519	−16
10	8	3	5	9	8	2	6	38 264.933*	38 264.930	−96*	−0.541	− 9
25	10	15	−5	25	10	16	−6	30 664.264	30 664.226	0	−0.055	+ 5
31	13	18	−5	31	13	19	−6	31 643.435	31 643.346	+2	−0.133	+ 2
37	16	21	−5	31	16	22	−6	30 780.403	30 780.255	−1	−0.222	0
20	12	8	+4	20	11	9	+2	33 581.695	33 581.781	−5	+0.095	+10
20	12	9	+3	20	11	10	+1	34 116.620	34 116.699	+3	+0.157	+ 7
21	11	11	0	21	10	12	−2	30 257.400	30 257.457	−2	+0.086	+ 1
21	12	10	+2	21	11	11	0	33 455.463	33 455.539	+1	+0.127	+ 6
23	13	11	+2	23	12	12	0	36 120.020	36 120.104	0	+0.142	+ 8
24	13	12	+1	24	12	13	−1	35 481.830	35 481.915	−4	+0.131	+16
25	13	13	0	25	12	14	−2	35 104.368	35 104.438	+1	+0.106	+ 1
26	14	12	+2	26	13	13	0	35 538.971	35 539.080	−2	+0.161	− 8
27	14	13	+1	27	13	14	−1	32 618.038	32 618.164	0	+0.190	+ 5
28	12	16	−4	28	11	17	−6	28 019.612	28 019.573	+6	−0.058	+ 3
29	15	14	+1	29	14	15	−1	35 447.767	35 447.898	+5	+0.195	− 3
30	15	15	0	30	14	16	−2	31 907.721	31 907.857	−4	+0.204	+ 2
32	14	18	−4	32	13	19	−6	29 238.917	29 238.879	−6	−0.055	+ 7
32	15	17	−2	32	14	18	−4	26 611.816	26 611.877	−1	+0.088	−16
32	16	16	0	32	15	17	−2	34 686.655	34 686.801	+2	+0.218	− 3
33	16	17	−1	33	15	18	−3	31 017.460	31 017.593	−4	+0.200	+ 3
34	16	18	−2	34	15	19	−4	28 502.438	28 502.522	−10	+0.124	− 8
35	15	20	−5	35	14	21	−7	34 699.523	34 699.457	+2	−0.100	− 2
35	16	19	−3	35	15	20	−5	28 215.162	28 215.193	+3	+0.048	+ 6
35	17	18	−1	35	16	19	−3	33 602.073	33 602.224	−2	+0.227	+ 4
36	17	19	−2	36	16	20	−4	30 558.060	30 558.168	+2	+0.163	+ 1
37	18	19	−1	37	17	20	−3	36 300.377	36 300.542	+1	+0.248	+ 2
38	18	20	−2	38	17	21	−4	32 778.179	32 778.309	+2	+0.196	+ 3
39	17	22	−5	39	16	23	−7	35 536.973	35 536.907	0	−0.098	+ 6
39	18	21	−3	39	17	22	−5	31 145.476	31 145.532	−5	+0.079	−19
40	19	21	−2	40	18	22	−4	35 157.858	35 158.010	+4	+0.230	+ 7

Table 4. Internal rotation parameters of α-picoline-N-oxide.

Parameter	Preliminary fit	Final fit
Fourier coefficient w_1 $[10^{-4}]$	−0.1058 (19)	−0.1060 (19)
angle ε [degrees]	26.2 (8)	25.2 (5)
moment of inertia I_α [amu · nm^2]	0.0330 (13)	0.0312 fixed
barrier height V_3 [kcal/mol]	2.155 (88)	2.278 (6)
reduced internal rotational constant F [GHz]	156 (6)	165.348 (9)
reduced barrier height s []	64.22 (16)	64.20 (16)
standard deviation σ [kHz]	7.9	8.0

Table 5. Observed unsplit lines of α-picoline-N-oxide. ν frequency, $\delta\nu$ deviation from calculated value, calculated with constants from Table 6.

J'	K'_-	K'_+	τ'	−	J''	K''_-	K''_+	τ''	ν/MHz	$\delta\nu$/kHz
7	0	7	−7		6	1	6	−5	20 908.890	+ 3
7	1	7	−6		6	1	6	−5	20 911.312	0
7	0	7	−7		6	0	6	−6	20 917.710	0
7	1	7	−6		6	0	6	−6	20 920.131	− 4
8	0	8	−8		7	1	7	−6	23 703.770	− 4
8	1	8	−7		7	1	7	−6	23 704.417	− 2
8	0	8	−8		7	0	7	−7	23 706.198	0
8	1	8	−7		7	0	7	−7	23 706.839	− 4
9	0	9	−9		8	1	8	−7	26 495.996	− 3
9	1	9	−8		8	1	8	−7	26 496.166	− 1
9	0	9	−9		8	0	8	−8	26 496.637	− 7
9	1	9	−8		8	0	8	−8	26 496.807	− 4
9	2	8	−6		8	1	7	−6	29 275.581	− 3
10	0	10	−10		9	1	9	−8	29 287.58*	+26
10	1	10	−9		9	1	9	−8	29 287.593	− 4
10	0	10	−10		9	0	9	−9	29 287.733	+12
10	1	10	−9		9	0	9	−9	29 287.769	+ 5
11	0	11	−11		10	1	10	−9	32 078.982	+ 7
11	1	11	−10		10	1	10	−9	32 078.982	− 3
11	0	11	−11		10	0	10	−10	32 079.016	− 1
11	1	11	−10		10	0	10	−10	32 079.016	−12
11	1	10	−9		10	2	9	−7	34 827.601	− 2
11	2	10	−8		10	2	9	−7	34 828.430	+ 2
11	1	10	−9		10	1	9	−8	34 830.523	+ 1
11	2	10	−8		10	1	9	−8	34 831.355	+ 7
12	2	10	−8		12	1	11	−10	28 015.514	+ 1
12	3	10	−7		12	2	11	−9	28 023.438	− 5
14	3	11	−8		14	3	12	−9	30 240.837	− 9
14	3	11	−8		14	2	12	−10	30 241.582	+11
14	4	11	−7		14	3	12	−9	30 258.955	+ 5
17	5	12	−7		17	5	13	−8	31 482.167	− 9
20	7	13	−6		20	7	14	−7	31 730.642	− 2
21	11	11	0		21	10	12	−2	30 257.415	+13
34	15	19	−4		34	14	20	−6	29 873.225	−11
38	17	21	−4		38	16	22	−6	31 334.335	0
40	18	22	−4		40	17	23	−6	32 214.916	+10

tory accuracy, the moment of inertia of the methyl top, I_α. The line frequencies are presented in Table 3, and the determined parameters in Table 4. Table 5 contains frequencies of unsplit lines. The results of the centrifugal distortion analysis are summarized in Table 6.

Discussion

Concerning the ^{14}N quadrupole coupling constants, it can be stated that these are remarkably small, namely smaller than 1 MHz. This magnitude is usually encountered for positively charged nitrogen, such as in nitrates [11] or in isocyanides [12]. For PYROX, the molecular C_{2V} symmetry allows a comparison with pyridine, C_5H_5N. In terms of a Townes-Dailey analysis [13], we have the parameters i_c (ionicity of carbon-nitrogen bond), i_o (ionicity of oxygen-nitrogen bond), and i_π (excess population of p-orbital perpendicular to the molecular plane). We assume i_c to be equal for PYROX and pyridine, while the i_π's may differ. Taking the value for i_c from [14], i_o and i_π may be determined for PYROX. The procedure is as follows:

As stated in [14], the normalized valence orbitals of the nitrogen atom are labelled ψ_1 through ψ_4, with the new convention

$$\psi_1 \equiv \sqrt{(1-2/3)} \cdot \psi_s + \sqrt{(2/3)} \cdot \psi_{p_z} \qquad \text{(N-O-bond)}, \qquad (1\,a)$$

$$\psi_{2,3} \equiv \sqrt{(1/3)} \cdot \psi_s - \sqrt{(1/2)-1/3)} \cdot \psi_{p_z} \pm \sqrt{(1/2)} \cdot \psi_{p_x} \qquad \text{(C-N-bonds)}, \qquad (1\,b)$$

$$\psi_4 \equiv \psi_{p_y} \qquad (\pi\text{-bond}), \qquad (1\,c)$$

where the factors "1/3" arise from the s-character of the σ-bonds (exact sp^2-hybridization assumed). The population numbers of these orbitals are expressed as

$$n(\psi_1) = 1 + i_o, \quad n(\psi_{2,3}) = 1 + i_c, \quad n(\psi_4) = 1 + i_\pi .$$

Constants		Correlation matrix							
A/MHz	3524.9512 (3)	1.							
B/MHz	2278.3924 (2)	0.85	1.						
C/MHz	1395.7957 (2)	0.60	0.84	1.					
Δ_J/Hz	80.9 (11)	0.67	0.87	0.93	1.				
Δ_{JK}/Hz	85.3 (16)	0.36	0.31	−0.12	0.04	1.			
Δ_K/Hz	488.3 (20)	−0.11	−0.25	0.06	−0.05	−0.09	1.		
δ_J/Hz	27.46 (17)	0.42	0.33	−0.14	0.03	0.98	−0.80	1.	
δ_K/Hz	124.3 (11)	−0.40	−0.31	0.13	−0.03	−0.98	0.81	−0.99	1.

Table 6. Rotational and centrifugal distortion constants of α-picoline-N-oxide. Watson's A-reduction has been used.

The population numbers of the nitrogen orbitals are then

$$\begin{aligned} n(\psi_s) &= 1/3 \cdot (1+i_o) + 2/3 \cdot (1+i_c), \\ n(\psi_{p_x}) &= (1+i_c), \\ n(\psi_{p_y}) &= (1+i_\pi), \\ n(\psi_{p_z}) &= 2/3 \cdot (1+i_o) + 1/3 \cdot (1+i_c). \end{aligned}$$

We relate the experimental coupling constants to the quadrupole coupling constant per p-electron, $eQq_{210} \approx -9.38$ MHz [15], and obtain

$$\begin{aligned} \chi^+/eQq_{210} &= -1 \cdot n(\psi_{p_z}) + 1/2 \cdot n(\psi_{p_x}) + 1/2 \cdot n(\psi_{p_y}) \\ &= -2/3 \cdot i_o + 1/6 \cdot i_c + 1/2 \cdot i_\pi, \end{aligned} \tag{2a}$$

$$\begin{aligned} \chi^-/eQq_{210} &= 3/2 \cdot (n(\psi_{p_x}) - n(\psi_{p_y})) \\ &= 3/2 \cdot i_c - 3/2 \cdot i_\pi. \end{aligned} \tag{2b}$$

From these two equations, we get the relations

$$i_o = i_c - 1/2 \cdot (3\chi^+ + \chi^-)/eQq_{210}, \tag{3a}$$

$$i_\pi = i_c - 2/3 \cdot \chi^-/eQq_{210}. \tag{3b}$$

If we take i_c from pyridine, where it amounts to ~19%, and neglect screening effects, our experimental data for PYROX give

$i_o = 0.19 - 0.181 \approx +1\%$, and $i_\pi = 0.19 - 0.062 \approx 13\%$.

We find i_o to be almost zero, while i_π is much larger than in pyridine ($i_\pi \approx 3\%$). Obviously, the electronegativity of the positively charged nitrogen is higher than that of formally neutral nitrogen atoms. One might therefore increase i_c to, say, 25%, which would accordingly increase i_o and i_π (from 3a, b). In addition, we find a positive net charge for the nitrogen atom, which leads to an increased eQq_{210} via charge correction [13]. This increase can be estimated to about 10%, so that i_o is increased by 0.018, and i_π by 0.006. The refined result is $i_c = 25\%$ (assumed), $i_o \approx +9\%$, and $i_\pi \approx +20\%$.

For PICOX, because of the different position of the inertia axes only the value of χ_{cc} can directly be compared, and is found to differ substantially from that found for PYROX. However, a difference in the values of χ_{cc} of the same magnitude is found in the pair α-picoline [16] vs. pyridine. It is therefore probable that this difference can be attributed to an electronic effect of the methyl group. The effect corresponds to an increase of the π-excess of ~2% and may be attributed to hyperconjugation of the methyl group.

As far as the internal rotation parameters are concerned, several statements can be made. Firstly, the moment of inertia of the internal top with respect to its axis of rotation, I_α, is not satisfactorily determined. We therefore made the following assumption: if the only contribution to the inertia defect, $\Delta \equiv I_{aa} + I_{bb} - I_{cc}$, comes from the out-of-plane protons, then for a C_{3v} symmetric internal top its moment of inertia should equal Δ, which is easily calculated from the rotational constants. On fixing the internal top moment of inertia to this value, we found only minor variations of the other parameters. Secondly, the Fourier coefficient, w_1, and accordingly the (threefold) potential barrier to internal rotation, V_3, is much higher (2.277 kcal/mole) than in isoelectronic o-fluorotoluene (0.649 kcal/mole, [17]). Thirdly, the axis of internal rotation is inclined to the a principal axis of inertia by an angle ε fairly close to the corresponding angle for the methyl-carbon – ring-carbon bond. However, as the structure of PICOX is not yet well determined, we cannot be more definitive about this point.

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