Infrared and Raman Spectra of Phenylisocyanide $C_6H_5N \equiv C$

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Infrared and Raman spectra of phenylisocyanide have been recorded and a vibrational analysis attempted in three stages. First, the experimental results alone were used for assignment of all A_1-class and 5 B_1-class fundamentals. Secondly, 9 B_2-class and 1 A_2-class fundamentals were assigned using their spectral positions close to phenyl*cyanide* fundamentals as a criterium. Finally, the 2 unassigned B_1-fundamentals, the 2 unassigned B_2-fundamentals, and 1 of the 2 unassigned A_2-vibrations were inferred from a study of the remaining experimental material. The assigned 32 fundamentals are summarized in Tables 2 and 3. Their positions are very close to normal vibration frequencies of phenylcyanide (mostly within 1 %).

In literature only one experimental infrared (IR) spectrum (4000 – 667 cm⁻¹) of unstable, liquid phenylisocyanide $C_6H_5N \equiv C$ (I) has appeared.[1] No Raman (Ra) spectrum has been reported and no identification of normal vibrations has been published. In this paper we intend to verify the expected very close agreement between the normal vibration frequencies of I and of related phenylcyanide (II). We want to use the result as one argument in a discussion on the structure of I in a following paper.

INSTRUMENTATION AND PREPARATION

IR spectra of gaseous I were recorded at room temperature at $p \sim 1$ mmHg in a 1 m cell on a Perkin-Elmer 125 grating spectrophotometer from 4000 to 400 cm⁻¹, and on a Fourier spectrometer (FS-500) from 450 to 20 cm⁻¹ in a 6 m gas cell.[2] The IR spectrum of the pure liquid at 20° in a KBr cell with 0.012 mm spacing was recorded on the Perkin-Elmer 125 instrument from 4000 to 400 cm⁻¹. For the region 400 to 30 cm⁻¹ a Perkin-Elmer FIS-3 instrument was used, the sample now being a 20 % sufficiently stable solution of I in hexane. A polyethylene cell with 1 mm spacing was applied. Pure I undergoes chemical change in the He-Ne laser light of the Coderg PH-1 Ra instrument used for the Ra measurements. However, the above-mentioned 20 % solution proved to be stable for hours. The sample volume applied was 300 μl. Measurements were performed perpendicular to the laser beam, depolarization measurements being carried out by rotation of the polarization analyzer by 90°. In a majority of cases (Table 1) the polarization results were unambiguous.

Table 1. Observed vibrational spectra of phenylisocyanide, C_6H_5NC.

| | Infrared spectra at 20° | | | | | | Raman spectrum at 20° 20 % sol. in hexane | | |
| Band No. | Gas at 1 mmHg | | | Liquid | | Assignment[c] | | | |
	Position cm⁻¹	P,R sep. and type	Inten-sity[a]	Position cm⁻¹	Inten-sity[a]		Position cm⁻¹	Polar.	Inten-sity[a]
1	$3040-3110^d$		m	3060	m	A_1, ν_2, ν_3, ν_4	3078	pol.	s
2	»		m	3040	w	$B_2, \alpha_{25}, \alpha_{26}$	3047	depol.	w
3				2280	w				
4	2130		s	2120	s	A_1, ν_5	2126	pol.	vs
5				1950	w				
6				1880	w				
7				1795	w				
8				1745	w				
9				1670	w				
10	1600		m	1595	m	A_1, ν_6	1600	pol.	s
11				1585	m	B_2, α_{27}			
12				1500	w				
13	1489	ca.12,A	m	1485	s	A_1, ν_7	1487	pol?	w
14				1455	m	B_2, α_{28}			
15	1394		vw	1390	vw				
16				1325	vw	B_2, α_{29}			
17				1285	vw	B_2, α_{30}			
18				1240	vw		1244	pol?	vw
19	1193	ca.12,A	w	1185	m	A_1, ν_8	1190	pol.	vs
20	1170	ca.13,A	w	1165	m	A_1, ν_9	1168	pol.	vs
21				1155	vw	B_2, α_{31}			
22				1095	w				
23	1071	ca.9,B?	w	1070	m	B_2, α_{32}			
24	1029	ca.10,A?	w	1025	m	A_1, ν_{10}	1029	pol.	s
25				1010	w				
26				1000	vw	A_1, ν_{11}	1003	pol.	vs
27	913	?,C	s	910	m	B_1, ν_{18}			
28				880	vw				
29				840	vw	A_2, α_{15}			
30	770		vw	765	m	A_1, ν_{12}	770	pol.	s
31	756	ca.14,C	s	755	s	B_1, ν_{19}	757	depol?	vw
32	685	?,C	m	680	s	B_1, ν_{20}			
33				660	w				
34				620	vvw	B_2, α_{34}	621	depol.	w
35	510	?,C	m	510	m	B_1, ν_{22}	512	depol.	w
36				475	w	A_1, ν_{13}	473	pol.	m
37				470	vw				
38				327^b	w		329	depol.	m
39				312^b	w				
40	149	?,C	m	161^b	s	B_1, ν_{24}	164	depol.	s

[a] Estimated. w = weak, m = medium, s = strong, v = very. [b] 20 % solution in hexane.
[c] ν_i: pure experimental assignment. Species and ν_i notation in agreement with Ref. 6.
α_i: assignment by comparison with spectrum of C_6H_5CN.[5] Subindex i in agreement with Ref. 6. [d] Several, unidentified maxima.

Our sample of I was prepared according to Ref. 3. Its IR spectrum was consistent with the one earlier published.[1]

ANALYSIS OF SPECTRA

I has C_{2v} symmetry with a normal vibration distribution of A_1 (12, IR + Ra, A-type), A_2 (3, Ra), B_1 (7, IR + Ra, C-type), and B_2 (11, IR + Ra, B-type), the parentheses giving the number, spectral activity, and IR band fine-structure type of the fundamentals. From a microwave investigation [4] rotational constants were taken as $A = 5660$, $B = 1640$, and $C = 1271$ Mc/s. P, R separations of IR gas phase bands of 11, 9, and 16 cm^{-1} were calculated for A, B, and C type contours. Observed and assigned vibrational frequencies are given in Table 1. Bands Nos. 1, 4, 10, 13, 19, 20, 24, 30 were assigned as A_1-fundamentals because they correspond to Ra lines which are polarized and of medium or strong intensity (except band No. 13) and to IR (liq.) lines of medium or strong intensity. They all appeared in the IR gas spectrum, but their identification as A type bands was not always possible (Table 1). Bands Nos. 26 and 36 were adopted as A_1 fundamentals solely on the Ra criterium. Thus, the assignment of all 12 A_1 fundamentals has been reached ($\nu_2 - \nu_{13}$).

Bands Nos. 27, 31, 32, 35, and 40 were adopted as B_1-fundamentals mainly due to their appearance as C-type bands in the IR gas spectrum, and as medium or strong lines in the IR (liq.) spectrum. Bands Nos. 31, 35, and 40 also occurred as depolarized Ra-lines. Of the remaining depolarized Ra-lines (bands Nos. 2, 34, 38) band No. 2 must correspond to the 2 expected B_2-hydrogen stretching frequencies. It is an open question, whether bands Nos. 34 and 38 are B_1 and/or B_2-vibrations. They are less likely to be A_2-vibrations since they both appear in IR liq. Thus, 5 out of 7 expected B_1-fundamentals have been assigned.

Table 2 shows the close agreement between normal vibration frequencies, so far assigned, for I, and for II.[5] This agreement suggests that the mere appearance of a band in our experimental spectra of I unassigned above, but close to an assigned band in the spectrum of II, may be taken as a tentative assignment criterium. Bands assigned as fundamentals in this way which, of course, is second to our first assignment criterium, are in Table 1 denoted by their species and by α_i instead of ν_i for the sake of clarity. In this way, 9 out of 11 expected B_2-fundamentals were assigned $[\alpha_{25} - \alpha_{32}, (\alpha_{33}$ appears only in $C_6H_5C\equiv CH)$, and $\alpha_{34}]$. The assignment of band No. 29 as α_{15} assumes a sometimes occurring break-down of selection rules for liquids. Table 3 shows the satisfactory agreement obtained.

The 6 missing fundamental vibration frequencies are now γ_{17} and γ_{23} (B_1), γ_{35} and γ_{36} (B_2), and γ_{14} and γ_{16} (A_2). They must be looked for by analyzing the so far unassigned experimental bands Nos. 3, 5, 6, 7, 8, 9, 12, 15, 18, 22, 25, 28, 33, 37, 38, and 39 (Table 1). Bands Nos. 5 – 9 can be interpreted in close analogy with Ref. 6. 1950 (exp.) $= \gamma_{14} + \gamma_{17}$, 1880 (exp.) $= \gamma_{14} + \gamma_{18}$, and 1795 (exp.) $= \gamma_{14} + \alpha_{15}$ yields $\gamma_{14} = 967$ or 955 in agreement with ν_{14} of II (Table 3), ignoring anharmonicity effects. Correspondingly, $\gamma_{17} = 983$ or 995. 1745 (exp.) $= \alpha_{15} + \nu_{18} = 840 + 913 = 1753$. 1670 (exp.) $= \nu_{18} + \nu_{19} = 913 + 755 = 1668$. 1500 (exp.) $= \nu_{10} + \nu_{13} = 1029 + 475 = 1504$. 1390 (exp.) $= \nu_{18} + \nu_{13} = 913 + 475 = 1388$. 1240 (exp.) $= \nu_{12} + \nu_{13} = 770 + 473 = 1243$.

Table 2. Comparison of experimentally assigned fundamental frequencies in cm^{-1} of phenylisocyanide and of phenylcyanide.[5] ν_i notation as in Ref. 6.

	i	Phenylisocyanide	Phenylcyanide	Per cent deviation
A$_1$	2		3080	
In plane	3	} 3040 – 3110	3062	
	4		3042	
	5	2130	2232	5
	6	1600	1599	0.07
	7	1489	1492	0.2
	8[c]	1193	1192	0.2
	9	1170	1178	0.6
	10	1029	1027	0.2
	11	1003	1001	0.2
	12[c]	770	769	1.5
	13[c]	473	461	2.5
B$_1$	17	γ_{17}[b]	(989)	(2.0)
Out of	18	913	925	1.4
plane	19	756	758	0.4
	20	685	686	0.2
	(21)		Only in $C_6H_5C\equiv CH$	
	22[c]	510	548	7.5
	23[c]	γ_{23}[b]	172	(7)
	24	149[a]	162	9.1(0.07)

[a]IR gas. For a solution in hexane: 161 cm^{-1}. [b]γ_i's are normal vibration frequencies unassigned by the methods producing Tables 2 and 3. A tentative assignment of combination bands (see text) results in $\gamma_{17} = 1010$ and $\gamma_{23} = ca.$ 160 or 329. [c]Sensitive to substitution such as $C_6H_5CN \rightarrow C_6H_5F$.[5]

Table 3. Phenylcyanide fundamental frequencies[5] in cm^{-1} (ν_i) and fundamental frequencies (α_i) of phenylisocyanide as suggested by simple comparison. ν_i notation as in Ref 6.

	i	ν_i	α_i	Per cent deviation
B$_2$	25	3072	3040 – 3110	
In plane	26	3027		
	27	1584	1585	0.07
	28	1448	1455	0.5
	29	1337	1325	1.0
	30	1289	1285	0.3
	31	1163	1155	0.7
	32	1071	1070	0.1
	(33)		Only in $C_6H_5C\equiv CH$	
	34	629	620	1.5
	35	551	γ_{35}[a]	(0)
	36[b]	381	γ_{36}[a]	(15)
A$_2$	14	978	γ_{14}[a]	(1.0)
Out of	15	848	840	1.0
plane	16	401	γ_{16}[a]	

[a]Unassigned fundamental frequency γ_i. A tentative assignment of combination bands (see text) results in $\gamma_{35} = 551$, $\gamma_{36} = 329$, and $\gamma_{14} = 955$. [b]Sensitive to substitution.[5]

Since band No. 34 was assigned as a B_2-vibration α_{34}, it is tempting to assign band No. 38 at 329 to another B_2-vibration, γ_{35} or γ_{36}, and preferably the latter which is close to ν_{36} (at 381) in the spectrum of II. 1095 (exp.) can now be taken as $\nu_{12} + \gamma_{36} = 770 + 329 = 1099$. Band No. 25 at 1010 may be γ_{17} so that $\gamma_{17} = 995$ and $\gamma_{14} = 955$ (above) are the better choices. Setting band No. 28 at $880 = \gamma_{35} + \gamma_{36}$ means $\gamma_{35} = 551$, identical with γ_{35} in the spectrum of II. Band No. 33 at $660 = 2\gamma_{36} = 658$. Unassigned experimental bands Nos. 3, 37, 39 remain. The frequency ratio of the 2 latter is 3:2 suggesting their interpretation as first and second overtones of a fundamental at *ca.* 160, perhaps ν_{24} already assigned, or the so far unassigned γ_{23}. In Ref. 6, $\nu_{23} = \nu_{36}$ is assumed for the spectrum of $C_6H_5C \equiv CH$.

Following the same procedure, $\gamma_{23} = 329$. Finally, band No. 3 (2280 exp.) must be taken as $\nu_5 + \nu_{24} = 2280$ (exp.).

We have no suggestion whatsoever how to assign the last fundamental γ_{16}. Ref. 5 reports that this vibration is insensitive to substitution such as $C_6H_5CN \rightarrow C_6H_5F$. There is no observed band in our spectra closer to 400 than bands Nos. 37 and 38 at 470 and 329.

In summary, the vibrational spectra of phenylisocyanide may be assigned in very close agreement with the spectra of phenylcyanide.

DISCUSSION

The 3N-6 dimensional potential energy surfaces of phenylisocyanide and of phenylcyanide are, of course, not congruent. However, their *curvatures* in almost all 3N-6 separate points of normal coordinate null-values must be very much alike, the normal vibration frequencies being so close. Since major structural differences must mean less similarity of energy surface curvature we shall use the results of Tables 2 and 3 as one argument in favour of great structural resemblence of I and II assuming, in a forthcoming paper on the structure of I, equal phenyl ring structure in both molecules, presenting additional evidence for this.

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