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The Infrared Spectra of the 1-Propynyl Anion

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The structure of the 1-propynyl anion, whose electronic structure is anologous to that of acetonitrile $H_3C\text{-}C{\equiv}N$:, is represented by $H_3C\text{-}C{\equiv}C{:}^-$ (I) as a first approximation. Nest and Gremm[1] have measured the infrared spectra of the alkali acetilides of the R-C CM type, where R is H, CH_3 or C_6H_5 and where M is an alkali metal, in order to investigate the structure of those compounds on the basis of the C≡C stretching frequencies alone; they interpreted the decrease in the C C stretching frequencies from Li to Cs compounds in terms of an increase in the contribution of the $R\text{-}\overset{\cdot\cdot}{C}^-{=}C{:}$ structure in the resonance hybride. If so, the contribution of the $H_3C\text{-}\overset{\cdot\cdot}{C}^-{=}C{:}$ (II) structure in the 1-propynyl anion(I) would lead to a decrease not only in the C≡C stretching frequencies but also in the C–C stretching frequencies. Radionov *et al.*[2] have studied the infrared spectra of some lithium acetylides and observed the Li-C stretching frequencies in the 440—495 cm^{-1} region, suggesting the presence of a strong covalent character in the Li-C bond. The present paper will deal with the infrared spectra of the 1-propynyl sodium and potassium; except for the lithium compound, which is unsuitable, as has been shown above; we hope to obtain the normal frequencies and the force constants of the 1-propynyl anion and to obtain information concerning their structures.

The 1-propynyl sodium and potassium were prepared by the ordinary method. The infrared spectra were observed for both compounds in the region of 4000—200 cm^{-1} by Nujol or hexachloro-1,3-butadiene mull prepared in a gloved box. The observed frequencies were assigned on the basis of the C_{3v} symmetry; they are shown in Table 1. The C≡C stretching frequencies observed in both compounds differ slightly from that previously reported, *viz.*, 2032 cm^{-1} for the sodium salt and 2023 cm^{-1} for the potassium salt.[1] The normal frequencies of the 1-propynyl anion are listed in Table 2.

The force constants for the 1-propynyl anion were calculated on the assumption of the Urey-Bradley force field, in which F' (linear repulsive force constant) was assumed to be $-0.1\ F$(repulsive force constant), as usual. The atomic distances of the anion were assumed to be C–H=1.11 Å, C–C=1.46 Å, and C≡C=1.21 Å, while the valence angles were assumed to be tetrahedral for the CH_3 group and linear for the C–C C skeleton. For comparison, the force constants were also calculated, on the same assumption of force field, for acetonitrile and propyne, whose normal frequencies have been reported by Pace and Neo[3] and by Crawford[4] respectively, while the atomic

Table 1. The infrared spectra and assignments of $CH_3C{\equiv}CNa$ and $CH_3C{\equiv}CK$ (cm^{-1})

Obs. $CH_3C{\equiv}CNa$	Obs. $CH_3C{\equiv}CK$	Assign.
	3500 w	2852+2×340=3532
3340 w		2040+970+347=3357
2904 s	2905 s	CH_3 asym. str. *E*
2851 w	2852 m	CH_3 sym. str. A_1
2040 vw	2027 w	C≡C str. A_1
1436 s	1442 s	CH_3 asym. bend. A_1
1368 w	1368 w	CH_3 sym. bend. A_1
1316 w		970+347=1317
	1310 w	973+340=1313
970 w	973 w	CH_3 rock. *E*
922 m	915 s	C-C str. A_1
	884 w	
	678 vw	2×340=680
630 w	632 w	
347 m	340 m	C≡C-C bend. *E*

Table 2. The normal frequencies of $CH_3C{\equiv}C^-$ ion (cm^{-1})

Species		Mode	$CH_3C{\equiv}CNa$	$CH_3C{\equiv}CK$
A_1	ν_1	CH_3 str.	2851	2852
	ν_2	C≡C str.	2040	2027
	ν_3	CH_3 bend.	1368	1368
	ν_4	C-C str.	922	915
E	ν_5	CH_3 str.	2904	2905
	ν_6	CH_3 bend.	1436	1442
	ν_7	CH_3 rock.	970	973
	ν_8	C≡C-C bend.	347	340

Table 3. The force constants of $CH_3C{\equiv}CNa$, $CH_3C{\equiv}CK$, $CH_3C{\equiv}N$, and $CH_3C{\equiv}CH$ (md/Å)

	$CH_3C{\equiv}CNa$	$CH_3C{\equiv}CK$	$CH_3C{\equiv}N$	$CH_3C{\equiv}CH$
K(C-H)	4.280	4.284	4.480	4.364
K(C-C)	4.531	4.448	3.945	3.996
K(C≡X)	12.951	12.796	17.488	15.500
H(HCH)	0·407	0.403	0.394	0.397
H(CCH)	0.218	0.223	0.188	0.170
F(H···H)	0.082	0.082	0.071	0.116
F(C···H)	0.385	0.382	0.624	0.659
H(CCX)	0.165	0.160	0.203	0.201

X=C or N.

1) R. Nest and J. Gremm, *Z. Anorg. Allg. Chem.*, **325**, 62 (1963).
2) A. N. Rodionov, G. V. Timofeyuk, T. V. Talalaeva, D. N. Shigorin, and K. A. Kocheshkov, *Izv. Akad. Nauk. SSSR, Sen Khim.* **1965**, 42.
3) E. L. Pace and L. J. Noe, *J. Chem. Phys.*, **49**, 5317 (1968).
4) B. L. Crawford, *ibid.*, **8**, 526 (1940).

distances and valence angles have been reported by Costain.[5] The numerical calculation was carried out by means of computer program reported previously[6] using an electronic computer, HITAC 5020 E, of the Computer Center of Tokyo University. The force constants were fitted by the least-squares method; they are listed in Table 3. The calculated frequencies are in good agreement with the observed ones within the limit of ± 1 cm^{-1} in the two sets of the anion listed in Table 2, and also in the acetonitrile and propyne.

As is shown in Table 3, the C≡C stretching force constant of the 1-propynyl anion is considerably smaller than that of the propyne; it is possible that, because of the increase in the electronic repulsion and the decrease in the *s* character in the bonding, the C C bond in the 1-propynyl anion is less stable than that of the propyne, in which the *sp* hybridisation is postulated for the bonding in the C C bond.

One notices from Table 3 that the C–C stretching force constant of the 1-propynyl anion is larger than that of the acetonitrile or propyne, but that the C–H stretching force constant of the anion is smaller than that of the molecules. In acetonitrile, there is a significant contribution of the $H_3{}^+C{=}C{=}N{:}^-$ (III)[7] structure. For the 1-propynyl anion, however, we may not expect any important contribution of the $H_3{}^+C{=}C{=}C{:}^{--}$ (IV) structure in the resonance hybride because the uni-negative-charged carbon in the (I) structure is far less electronegative than the nitrogen atom in the acetonitrile and the distribution of the electronic charge in the (IV) structure is unfavorable. Accordingly, another important structure, $H_3{}^-C{=}C{=}C{:}$ (V), in which the negative charge is distributed among three hydrogen atoms, may be considered; its contribution may be more significant than that of the (III) structure in the acetonitrile.

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5) C. C. Costain, *ibid.*, **29**, 864 (1958).

6) T. Shimanouchi, "Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules," Tokyo Univ. (1968).

7) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York (1960), p. 269.