Detection of *C*-Cyanophosphaethyne, N≡C–C≡P, by Microwave Spectroscopy

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Summary The microwave spectrum of the new species *C*-cyanophosphaethyne N≡C–C≡P has been detected in the products of a gas phase high temperature (*ca.* 700 °C) reaction between cyanogen azide, NCN_3, and phosphaethyne, HC≡P; the new species which is the monophosphorus analogue of cyanogen, $(CN)_2$, has a dipole moment of 3·5 D.

RECENT studies have indicated that various substituted phospha-alkynes, RC≡P, where R is Me,[1] CF_3,[2] or F[3] can be made, and may have limited stability. As a natural sequel to this initial breakthrough into the study of the properties of the phospha-alkynes the pseudohalide CN group has been substituted in phosphaethyne. The methods have in general employed pyrolysis techniques[4] in which fragments such as H Hal (Hal = halogen) are eliminated from parent species to leave the required phospha-alkyne. Such a method has not proved feasible in this case because HCN tends to eliminate. An alternative route involving a direct reaction with HCP has been developed to detect and study N≡C–C≡P by microwave spectroscopy.

Apart from the inherent chemical interest in this new species the possibility of detecting interstellar N≡C–C≡P by radio astronomy has provided a strong incentive for this work.

The method used involved a double furnace system in which NCN_3 was pyrolysed in the presence of HCP, itself produced by pyrolysis of $MePCl_2$. NCN_3 produces high yields of radicals either on photolysis[5] or pyrolysis.[6] The species produced on photolysis are NCN, CN, N_3 as well as CNC[5] and in the presence of O_2, NCO is readily produced and with H_2O, HNCN. During photoelectron experiments on NCN_3[7] it was found that unless NCN_3 flowed rapidly through the ionisation chamber only the spectrum of $(CN)_2$ was detectable (unpublished). On this basis it seemed possible that in the presence of the copious supply of radicals obtainable from NCN_3 the H atom in HCP might be replaced by CN. It was not expected that this method would yield much NCCP but the microwave technique with its high sensitivity towards linear species with substantial dipole moments might still detect it. A comparison of the dipole moment in HCP with that in HCN indicated a dipole moment of *ca.* 2·5 D.

HCP was produced by flowing $MePCl_2$ at 20 μmHg pressure through a quartz tube (0·8 mm internal diameter) heated to 1000 °C over *ca.* 15 cm [reaction (1)].[8] After

$$\mathrm{MePCl_2} \xrightarrow{1000\,^{\circ}\mathrm{C}} \mathrm{HC{\equiv}P} + 2\mathrm{HCl} \qquad (1)$$

passing these products through a trap at −78 °C, filled with KOH pellets, NCN_3 was admixed to give a total pressure of *ca.* 50 μmHg and this mixture passed through a second furnace, heated to *ca.* 700 °C. The NCN_3 was made by reacting BrCN with solid NaN_3 overnight in a 5 l vessel in which it was stored.[7,9] The products were then passed through the cell of a Hewlett Packard microwave spectrometer operating between 26·5 and 40 GHz.

The spectrum consists of three groups of $\Delta J = +1$ transitions whose vibrational satellite patterns are characteristic of a linear molecule. The patterns were almost identical with that of cyanoethyne HC≡C–C≡N.[10] In particular there were two sets of l-doublets which indicated that the species has at least 4 atoms. Frequencies and rotational constants are given in the Table.

Table. Transition frequencies and rotational constants of NCCP

$J+1$	J	Frequency/MHz	o–c
5	←4	27044·707	0·012
6	←5	32453·587	0·010
7	←6	37862·442	0·015

$B_0 = 2704{\cdot}4803 \pm 0{\cdot}0019$ MHz
$D_0 = 0{\cdot}216 \pm 0{\cdot}013$ kHz

The B_0 value was within 5 MHz (0·2%) of the value (2709·9 MHz) predicted using the structural parameters: r(C≡N) = 1·159 and r(C–C) = 1·378 Å both from HC_3N[11] and r(C≡P) = 1·544 Å from $CH_3C≡P$.[1] This agreement is excellent and as no viable alternative linear species can be formed from H, C, P, and N with an acceptable B value we conclude that the spectrum belongs to NCCP. The presence of Cl can be discounted because this nucleus would cause observable hyperfine splittings.

The dipole moment is interesting in that it is quite large, 3·44 ± 0·03 D. It is not simply related to those of HCP (0·39 D)[12] and HCN (2·985 D)[13] as additive reasoning suggests a value of *ca.* 2·6 D, considerably smaller than the value observed, which is close to that of HC≡C–C≡N. The molecule is quite long and the dipole moment is a strong function of length as indicated by the series HCN : HC_3N : HC_5N for which it has the values 2·985 : 3·6 : 4·33 D, respectively.

No phosphorus-containing molecule has been detected in the interstellar medium although one would expect HCP and PH_3 to be likely contenders. As their dipole moments are not large (nearly a factor of 10 smaller than that of NCCP) the dipole dependent part of the interstellar intensity factor is *ca.* 100 times greater for NCCP.

The abundance of the longer carbon chain species[14] in certain interstellar clouds strongly suggests that such species as N≡C–C≡N and N≡C–C≡C–C≡N are also present. Consequently it seems likely that NCCP may be present and detectable by radio astronomy.

This detection of NCCP opens up the possibility that other pseudohalide substituted phosphaethyne species may be made. The spectrum is not strong and this implies that it is only a minor constituent in this system, perhaps only of the order of 1%.

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