Spectra attributed to the PCN and HPCN Free Radicals

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WE have reported[1] that the NCN and HNCN free radicals are produced in the flash photolysis of ammonia–cyanogen mixtures. The mechanism suggested was

$$CN(X\,^2\Sigma) + NH(X\,^3\Sigma) \rightarrow$$
$$H(^2S) + NCN(^3\Sigma_g^-, {}^1\Delta_g) \xrightarrow{M} HNCN(X\,^2A'')$$

the NH radical being produced mainly by successive reaction of CN with NH_3 and NH_2. Since similar reactions would be expected to occur between CN and PH, we have studied the flash photolysis of PH_3–C_2N_2–N_2 mixtures and report two new absorption spectra which can be attributed to the PCN and HPCN free radicals.

Cyanogen was prepared by the reaction of potassium cyanide with copper sulphate,[2] and phosphine (Matheson) was purified by distillation *in vacuo*. A mixture of PH_3–C_2N_2–N_2 (0·2 : 50 : 200 mm. Hg pressure) was flash photolysed at an energy of ~1000 J. The electronic absorption spectra were recorded on Ilford HP3 plate using a Hilger quartz spectrograph, model E742, with an absorption path of 50 cm. The PCN spectrum rises to a maximum intensity of ~3 μsec. and is visible for ~150 μsec. Similar behaviour was observed for the HPCN spectrum, the overall intensity of which was increased by using 0·3 : 80 : 170 mm. Hg pressure of PH_3–C_2N_2–N_2.

The first spectrum consists of two bands with prominent triplet *Q*-heads, the strongest band near 3014 Å and the other near 2857 Å (Tables 1 and 2), and is assigned to PCN. The absence of hydrogen is proved by the fact that the same spectrum is obtained from PCl_3–C_2N_2–N_2 mixtures and the structure PCN is preferred to that of CNP by its mode of formation and by analogy with the NH_3–C_2N_2–N_2 system where only NCN is observed. The sub-bands near 3014 Å are attributed to the

TABLE 1

Wavelengths of intensity maxima in the 3014 Å *band of* PCN

λ_{air}(Å)	ν_{vac}(cm.$^{-1}$)
3056·4	32709
3040·4	32881
3030·6	32987
3029·4	33000
3024·0	33059
3020·2	33101
3019·1	33113
3018·2	33123
3014·4	33165
3008·6	33228
3005·1	33267
3002·5	33296
3000·4	33319
2999·6	33328
2998·2	33344
2996·9	33358
2994·4	33386
2993·0	33402
2990·4	33431
2989·3	33443
2980·4	33543
2966·2	33703

TABLE 2

Q Heads of PCN [$^3\Pi(a)$–$^3\Sigma^-$]

Band	Sub-band	λ_{air}(Å)	ν_{vac}(cm.$^{-1}$)	$\Sigma\nu$(cm.$^{-1}$)
3014 Å	$^3\Pi_2$–$^3\Sigma^-$	3024·0	33059	
				106
	$^3\Pi_1$–$^3\Sigma^-$	3014·4	33165	
				102
	$^3\Pi_0$–$^3\Sigma^-$	3005·1	33267	
2857 Å	$^3\Pi_2$–$^3\Sigma^-$	2865·5	34888	
				106
	$^3\Pi_1$–$^3\Sigma^-$	2856·8	34994	
				103
	$^3\Pi_0$–$^3\Sigma^-$	2848·4	25097	

000–000 band of a $^3\Pi(a)$–$^3\Sigma^-$ transition of the linear PCN by analogy with NCN ($^3\Pi_u \leftarrow {}^3\Sigma_g^-$).[3] It is likely that the 2857 Å band is due to vibrational excitation in the ν_1 or ν_3 mode of the upper electronic state in view of the relatively large separation between the two bands (~1830 cm.$^{-1}$). The larger triplet splitting for PCN (~104 cm.$^{-1}$), as compared with the triplet splitting of ~40 cm.$^{-1}$ for NCN, is expected for the heavier molecule because of increased spin–orbit interaction.

The second spectrum consists of two weak and diffuse multiple sub-band systems, one near 3360 Å and the other near 3160 Å (Table 3), the appearance of which is very similar to the perpendicular band of the 3440 Å system of HNCN ($\tilde{A}^2A' \leftarrow \tilde{X}^2A''$) analysed by Herzberg and Warsop.[4]

TABLE 3

Wavelength of HPCN *bands*

System	λ_{air}(Å)	ν_{vac}(cm.$^{-1}$)	$\Delta\nu$(cm.$^{-1}$)
a	3377	29604	
			114
	3364	29718	
			89
	3354	29807	
b	3187	31368	
			139
	3173	31507	
			109
	3162	31616	
			91
	3153	31707	
			101
	3143	31808	

The carrier of the second spectrum is assigned to HPCN by analogy with HNCN and because the spectrum was absent in the flash photolysis of the PCl_3–C_2N_2–N_2 mixture.

In view of the observed presence of other (unidentified) species in the ammonia–cyanogen system, both assignments must be considered as tentative in the absence of a complete spectroscopic analysis.

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[4] G. Herzberg and P. A. Warsop, *Canad. J. Phys.*, 1963, **42**, 286.