

A Theoretical Comparison of Phosphino and Amino Groups in the Isocyanide–Cyanide Rearrangement

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Ab initio molecular orbital calculations have been used to study the isocyanide–cyanide rearrangement involving the migration of the hydrogen, amino and phosphino groups. Geometries were optimized using MP2/6-311G(d,p) while relative energies were obtained from CISDQ/6-311++G(d,p) wavefunctions. Structures and some spectroscopic properties of the equilibrium structures are predicted. Phosphinoisocyanide is found to lie 16 ± 2 kcal mol⁻¹ above phosphinocyanide, and to rearrange to the latter with an energy barrier of 27 ± 2 kcal mol⁻¹. Energetics (kcal mol⁻¹) of two other rearrangements are as follows: isocyanamide (0) \longrightarrow TS (37) \longrightarrow cyanamide (-44) and hydrogen isocyanide (0) \longrightarrow TS (30) \longrightarrow hydrogen cyanide (-14). Phosphinoisocyanide exhibits kinetic and thermodynamic stability similar to hydrogen isocyanide (relative to their isomers) and should thus be detectable in both gaseous and condensed phases.

There has been increasing interest in the use of isocyanides (R–N \equiv C) as reactive intermediates in organic synthesis and as ligands in complexation to transition metals.¹ The cyanide–isocyanide rearrangement has been shown to be involved in several of these transformations.² Isocyanides are able to act as bases forming hydrogen-bonded complexes with various hydrogen-containing compounds.³ Isocyanides are also susceptible to attack by nucleophiles, electrophiles and radicals giving imines as primary products.⁴ The addition can, under certain conditions, be stereospecific depending on the nature of the attacking agent. The molecular structures of some aliphatic and aromatic isocyanides have been determined by microwave spectrometry.⁵ Nevertheless, stable isocyanides which carry a first-row heteroatom on nitrogen are rather rare, presumably because they rearrange rapidly to the corresponding cyanides. Substituted isocyanamides (PhHN–N \equiv C) and fulminates (Ar–O–N \equiv C) generated by flash vacuum pyrolysis were found to undergo isomerization at very low temperatures (-100 °C) or polymerization at slightly higher temperatures (-80 °C).⁶ This instability which is a common property of many heteroatom-substituted cumulenes appears to be a consequence of the rather weak N–N and N–O bonds.

Previous *ab initio* molecular orbital calculations⁷ predicted that isocyanamide (H₂N–N \equiv C) lies about 45 kcal mol⁻¹ higher in energy than cyanamide (H₂N–C \equiv N). The latter value is in fact much larger than the corresponding energy difference of 15 and 24 kcal mol⁻¹ in the HNC–HCN and H₃CNC–H₃CCN systems, respectively. In contrast, silyl isocyanide (H₃SiNC) has been calculated to be only 7 kcal mol⁻¹ above its cyanide isomer⁸ (H₃SiCN, at the MP2/DZP level of theory).

In view of these results, the possible stabilizing effect of a phosphino group on isocyanides is of particular interest bearing in mind that the analogous amino-isocyanides (isocyanamides) are much less stable than the aminocyanides (cyanamides). To investigate this effect, we have calculated the potential energy surfaces of the simplest isocyanamide–cyanamide (H₂N–NC \longrightarrow H₂N–CN) and phosphinoisocyanide–phosphinocyanide (H₂P–NC \longrightarrow H₂P–CN) rearrangements using *ab initio* molecular orbital methods. We have found that phosphinoisocyanide has a lower relative energy than methyl isocyanide as compared with their corresponding isomers. For the purpose of comparison the calculated results

obtained for the parent HNC \longrightarrow HCN rearrangement are also reported in the present paper.

Calculations and Results

The geometries of stationary points were initially optimized at the Hartree–Fock (HF) level with the 6-31G(d) basis set, then reoptimized at both Hartree–Fock and second-order Møller–Plesset perturbation theory (MP2) levels with the 6-31G(d,p) basis set and finally determined at the MP2 level with the 6-311G(d,p) basis set. Harmonic vibrational wavenumbers were calculated at the HF/6-31G(d,p) level in order to characterize stationary points and to estimate zero-point vibrational energies (E_{zp}). Improved relative energies were calculated as single points at the levels of full fourth-order Møller–Plesset perturbation theory and configuration interaction (CISDQ) using the 6-311++G(d,p) basis set (++ denotes a set of diffuse sp-functions on C, N and P and s-functions on H) and MP2/6-311G(d,p)-optimized geometries. For the CHN system, to test further the effect of the basis set on relative energies, configuration interaction calculations (CISDQ) employing larger basis sets including f-functions were also performed. Some electronic properties were computed using MP2/6-311G(d,p) wavefunctions.

All of the calculations were carried out with the aid of the local versions of the GAUSSIAN 88⁹ and CADPAC¹⁰ programs.

Geometrical parameters optimized at the different levels for the equilibrium structures including isocyanamide **1**, cyanamide **2**, phosphinoisocyanide **3** and phosphinocyanide **4** and the transition structures for rearrangement **5** and **6**, shown in Fig. 1, are listed in Table 1. The predicted geometries and rotational constants of four equilibrium structures **1–4** are summarized in Table 2. Corresponding total and relative energies of the CH₂N₂ structures **1**, **2** and **5** and CH₂PN structures **3**, **4** and **6** calculated at various levels of accuracy are recorded in Tables 3 and 4, respectively. Table 5 gives the energetics of the parent HNC–HCN system. The atomic charges and dipole moments are collected in Table 6. Fig. 2 displays the calculated infrared (IR) spectra of both phosphino molecules **3** and **4**. The wavenumbers and intensities were calculated using HF/6-31G(d,p) wavefunctions. The wavenumbers were then systematically scaled by 0.9 to take into account the overestimation of vibrational frequencies at this level of accuracy. This correction should

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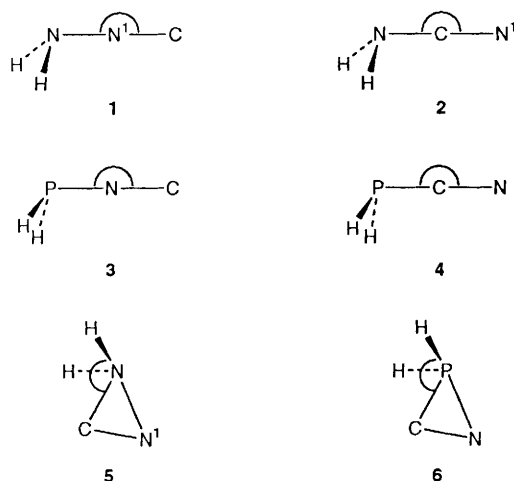


Fig. 1 Equilibrium (1–4) and transition (5, 6) structures considered

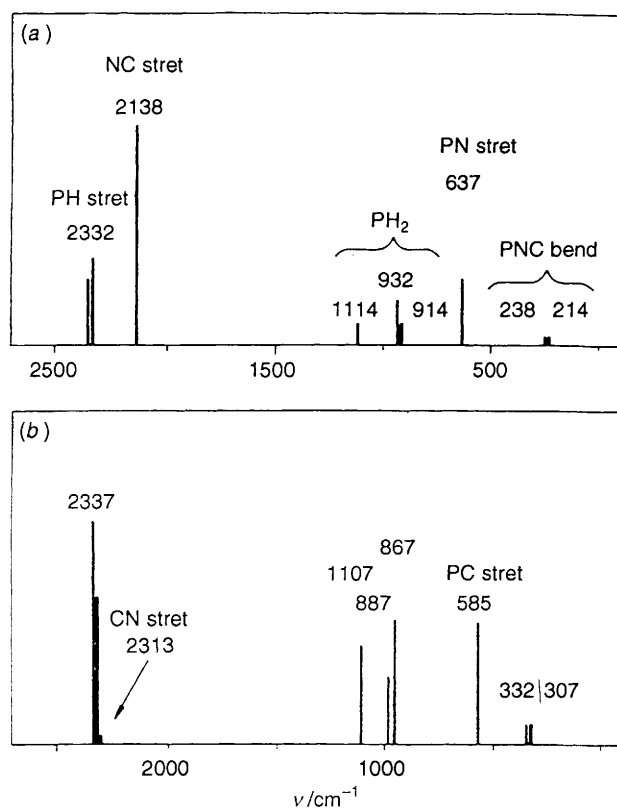


Fig. 2 Calculated infrared spectra of (a) phosphinoisocyanide (3) and (b) phosphinocyanide (4). Intensities are normalized to the largest value. Only fundamental bands are given. Wavenumbers are calculated at the HF/6-31G(d,p) level and scaled by 0.9.

provide a semi-quantitatively correct picture of the IR spectra considered. Fig. 3 presents a correlation diagram of molecular orbitals in three different isocyanide–cyanide pairs. Schematic energy profiles showing the rearrangement and dissociation reactions are shown in Fig. 4.

Throughout this paper, bond distances are given in Å, bond angles in deg, total energies in hartree (E_h) and relative energies, unless otherwise noted, in kcal mol⁻¹.

Discussion

Equilibrium Structures.—Compared with the HF-values, a systematic lengthening of bonds occurs upon incorporation of

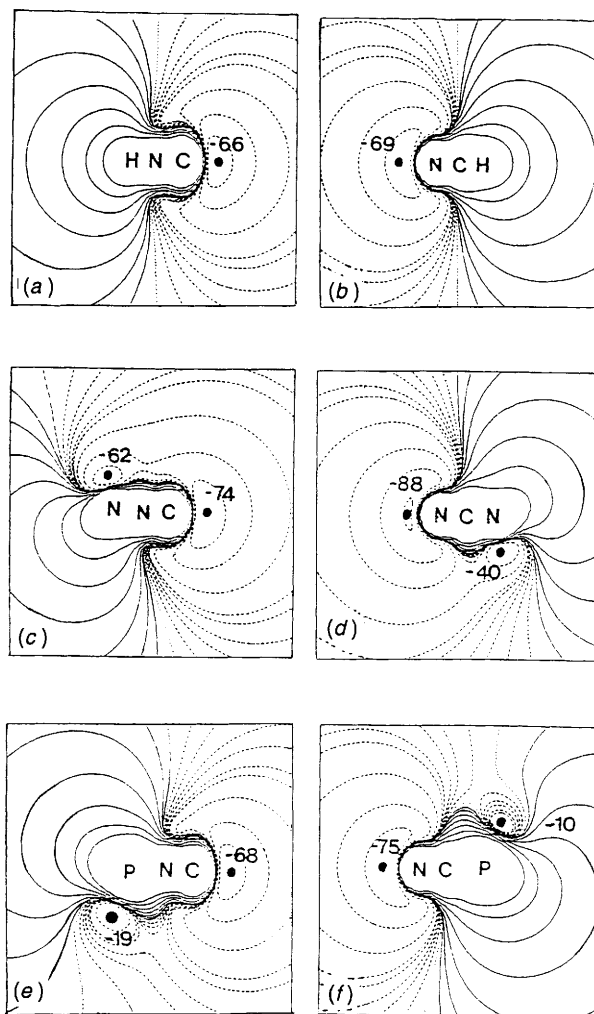


Fig. 3 Molecular electrostatic potential maps calculated at the HF/6-311 + G(d,p) level: (a) HNC, (b) HCN, (c) H₂NNC (1), (d) H₂NCN (2), (e) H₂PNC (3) and (f) H₂PCN (4). Isocontours and potential minima are given in 10⁻³ au. The isopotential contours have values of 80, 40, 20, 10, 5, 2.5, 1.25, 0.0, -1.25, -2.5, -5, -6, -10, -20, -40 and -60 (10⁻³ au). ● indicates the potential minima.

electron correlation at the MP2 level, in particular for the multiple bonds. The values obtained at both MP2/6-31G(d,p) and MP2/6-311G(d,p) levels are also similar.

The rotational spectra of both isocyanamide **1** and cyanamide **2** molecules have been reported.^{11,12} Some geometric parameters of cyanamide **2** have thereby been determined assuming a linear N–C–N framework.¹¹ For isocyanamide **1**, only the rotational constants of both inversion states O⁺ and O⁻ are available.¹² There have also been a couple of previous theoretical studies^{13,14} of the structures of both CH₂N₂ isomers using HF calculations with small basis sets. It has recently been shown¹⁵ that the bond distances (r_e) of isocyanides and cyanides are systematically underestimated and overestimated at the HF/6-31G(d,p) and MP2/6-31G(d,p) levels, respectively, so that the mean of both HF and MP2 values of a distance provides a good estimate of the experimental value (r_o). We have verified that this simple correction scheme actually holds for all three bond distances of cyanamide **2**. As seen in Table 2, for each of the bond distances of **2**, the average of both HF/6-31G(d,p) and MP2/6-31G(d,p) values compares well with the corresponding experimental one. Therefore, we have adopted these empirically adjusted values as the predicted bond lengths for the remaining molecules **1**, **3** and **4**.

Table 1 Optimized equilibrium structures (1–4) and transition structures (5, 6)

Parameter ^a	HF/6-31G(d)	HF/6-31G(d,p)	MP2/6-31G(d,p)	MP2/6-311G(d,p)
Isocyanamide (1)				
C–N ¹	1.153	1.153	1.191	1.186
N–N ¹	1.355	1.353	1.364	1.358
N–H	1.001	1.000	1.014	1.016
∠ NNC	175.6	175.8	174.7	174.6
∠ HNN	108.3	108.6	107.7	107.9
∠ HNH	109.2	109.7	108.5	108.8
Cyanamide (2)				
C–N ¹	1.138	1.138	1.181	1.173
C–N	1.344	1.341	1.355	1.357
N–H	0.998	0.996	1.010	1.012
∠ NNC	178.1	178.3	177.2	176.8
∠ HNC	114.5	114.9	113.1	112.3
∠ HNH	113.1	114.0	111.6	111.4
Phosphinoisocyanide (3)				
C–N	1.160	1.160	1.193	1.188
P–N	1.714	1.714	1.727	1.726
P–H	1.399	1.402	1.404	1.407
∠ PNC	173.5	172.2	173.7	173.5
∠ HPN	97.2	97.4	96.1	95.8
∠ HPH	95.0	95.6	94.4	94.1
Phosphinocyanide (4)				
C–N	1.137	1.137	1.182	1.177
P–C	1.802	1.805	1.789	1.789
P–H	1.398	1.402	1.404	1.408
∠ PCN	176.3	175.6	174.5	174.2
∠ HPC	96.0	96.4	95.4	94.9
∠ HPH	96.0	96.1	95.4	94.7
Transition structure (5): (1) → (2)				
C–N ¹	1.195	1.195	1.202	1.196
C–N	1.565	1.561	1.655	1.649
N–N ¹	1.866	1.868	1.897	1.893
N–H	1.000	0.999	1.014	1.015
∠ NCN ^{1b}	84.0	84.3	81.6	81.8
∠ NN ¹ C ^b	56.4	56.2	59.6	59.6
∠ HNC	104.7	104.2	97.1	97.2
∠ HNH	110.6	111.0	109.3	109.5
Transition structure (6): (3) → (4)				
C–N	1.168	1.168	1.201	1.197
P–C	2.002	2.002	2.003	2.018
P–N	2.192	2.192	2.124	2.134
P–H	1.397	1.397	1.403	1.406
∠ PCN ^b	83.0	83.0	78.7	78.7
∠ PNC ^b	65.1	65.1	67.6	68.0
∠ HPC	90.0	90.0	88.6	87.8
∠ HPH	95.2	95.3	94.8	94.1

^a See atom numbering in Fig. 1. ^b Non-independent parameters.

In contrast, it is also known¹⁶ that the bond angles around multiply bonded nitrogen atoms are not well reproduced by HF-wavefunctions. For these geometric parameters, the MP2 calculations yield values much closer to the observed ones. Therefore we have chosen the mean of both MP2/6-31G(d,p) and MP2/6-311G(d,p) values optimized for each bond angle considered as our predicted value. In this way, we have obtained a full set of predicted geometrical parameters for isocyanamide **1**, cyanamide **2**, phosphinoisocyanide **3** and phosphinocyanide **4**. These predicted geometries allow the evaluation of rotational constants (A_0 , B_0 , C_0). These results are shown in Table 2. For both amino molecules **1** and **2**, the predicted rotational constants compare favourably with those derived from microwave spectrometry.^{11,12} The larger deviation of the calculated A_0 constant in isocyanamide **1** is likely to arise from a small

overestimation of the HNN bond angle ($< 1^\circ$). An earlier MO study¹⁴ reported the values of $A_c = 294\,446$ and $317\,720$ MHz for isocyanamide **1** and cyanamide **2**, respectively. It appears that the latter values are too large. The splitting of both B_0 and C_0 rotational constants in both phosphino molecules **3** and **4** is predicted to be quite small ($B_0 - C_0 \approx 30$ MHz). However, such a value is consistent with that of 24 MHz experimentally¹⁷ determined for phosphinoacetylene **7**.

It is worth noting the geometry of the phosphino group in **7** determined by microwave spectrometry¹⁷: $\angle \text{HPC} = 96.9^\circ$, $\angle \text{HPH} = 93.9^\circ$, $\angle \text{PCC} = 173 \pm 2^\circ$, $r(\text{P-H}) = 1.414$ Å and $r(\text{P-C}) = 1.77$ Å. These values are consistent with the predicted values for the analogous phosphino groups in **3** and **4**. It appears that the P–A≡B skeleton in phosphino molecules shows a larger deviation from the linearity (about 7°) than does the

Table 2 Predicted geometrical parameters and rotational constants of equilibrium structures

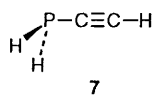
Parameter ^a	Predicted ^b (<i>r</i> ₀)	Exptl ^c (<i>r</i> ₀)	Parameter	Predicted ^b (<i>r</i> ₀)
H₂NNC (1)			H₂PNC (3)	
N–C	1.172		N–C	1.177
N–N	1.359		P–N	1.721
N–H	1.007		P–H	1.403
∠ NNC	174.7		∠ PNC	173.6
∠ HNN	107.8		∠ HPN	96.0
∠ NHN	108.6		∠ HPH	94.2
<i>A</i> ₀	286 938	282 757	<i>A</i> ₀	132 774
<i>B</i> ₀	10 806	10 757	<i>B</i> ₀	5 891
<i>C</i> ₀	10 595	10 525	<i>C</i> ₀	5 859
<i>B</i> ₀ – <i>C</i> ₀	211	232	<i>B</i> ₀ – <i>C</i> ₀	32
H₂NCN (2)			H₂PCN (4)	
C–N	1.160	1.160	C–N	1.160
N–C	1.348	1.346	P–C	1.797
N–H	1.003	1.001	P–H	1.403
∠ NCN	177.0	(180) ^d	∠ PCN	174.3
∠ HNC	112.7	—	∠ HPC	95.2
∠ HNH	111.6	113.5	∠ HPH	95.1
<i>A</i> ₀	304 565	—	<i>A</i> ₀	132 381
<i>B</i> ₀	10 151	10 129	<i>B</i> ₀	5 254
<i>C</i> ₀	9 926	9 866	<i>C</i> ₀	5 225
<i>B</i> ₀ – <i>C</i> ₀	225	263	<i>B</i> ₀ – <i>C</i> ₀	29

^a Rotational constants in MHz. ^b Means of both HF/6-31G(d,p) and MP2/6-31G(d,p) values for bond distances and means of both MP2/6-31G(d,p) and MP2/6-311G(d,p) values for bond angles: see text. ^c Taken from ref. 12 for H₂NNC and ref. 11 for H₂NCN. ^d Assumed value.

Table 3 Calculated total energies for six stationary points considered

Method ^a //Geometry ^b	H ₂ NNC (1)	H ₂ NCN (2)	TS: 1 → 2 (5)	H ₂ PNC (3)	H ₂ PCN (4)	TS: 3 → 4 (6)
HF/6-31G(d)//HF/6-31G(d)	-147.839 21	-147.908 66	-147.771 28	-434.162 23	-434.180 48	-434.106 52
MP2/6-31G(d)//HF/6-31G(d)	-148.269 45	-148.345 97	-148.199 41	-434.526 32	-434.558 07	-434.481 97
MP4SDQ/6-31G(d)//HF/6-31G(d)	-148.289 71	-148.360 88	-148.225 16	-434.555 46	-434.582 62	-434.509 42
HF/6-31G(d,p)//HF/6-31G(d,p)	-147.846 59	-147.916 93	-147.778 88	-434.166 42	-434.184 70	-434.109 44
MP2/6-31G(d,p)//MP2/6-31G(d,p) ^c	-148.303 82	-148.382 05	-148.231 69	-434.567 28	-434.601 14	-434.521 15
MP2/6-311G(d,p)//MP2/6-311G(d,p) ^c	-148.415 00	-148.491 02	-148.344 51	-434.771 99	-434.805 69	-434.727 79
MP2/6-311 + + G(d,p)//MP2/6-311G(d,p)	-148.355 50	-148.432 71	-148.286 15	-434.616 09	-434.649 23	-434.572 30
MP3/6-311 + + G(d,p)//MP2/6-311G(d,p)	-148.361 92	-148.432 69	-148.297 07	-434.632 70	-434.658 60	-434.587 96
MP4SDQ/6-311 + + G(d,p)//MP2/6-311G(d,p)	-148.372 96	-148.443 43	-148.307 91	-434.644 92	-434.671 14	-434.598 86
MP4SDTQ/6-311 + + G(d,p)//MP2/6-311G(d,p)	-148.396 62	-148.468 04	-148.333 10	-434.665 40	-434.693 93	-434.621 46
CISD/6-311 + + G(d,p)//MP2/6-311G(d,p)	-148.317 57	-148.388 26	-148.251 11	-434.594 02	-434.617 08	-434.545 71
CISDQ/6-311 + + G(d,p)//MP2/6-311G(d,p) ^d	-148.374 28	-148.444 48	-148.312 22	-434.647 06	-434.673 22	-434.602 46
<i>E</i> _{zp} ^e	20.8	20.9	18.8	15.5	15.8	14.6

^a Core orbitals are frozen unless otherwise noted. ^b Using optimized geometries given in Table 1. ^c Full set of MOs employed in MP2 calculations. ^d Including corrections for quadruple substitutions. ^e Zero-point vibrational energies calculated at the HF/6-31G(d,p) level and scaled by 0.9 to account for systematic overestimation; in kcal mol⁻¹.



N–A≡B in amino molecules (about 3°). In both isocyanides or in cyanides, the triply bonded C≡N moiety has a similar distance. Electron diffraction measurements¹⁸ of the structure of methylphosphine (CH₃PH₂) gave a P–C bond length of 1.858 Å. There is thus a shortening of the P–C distance (up to 0.09 Å) upon formation of a triple bond at carbon. A similar trend holds for the P–N distance where the normal P–N single bond length is about 1.77 Å. This is overall consistent with the trend seen for isocyanamide **1** and cyanamide **2**.^{11,12}

The calculated infrared intensities (Fig. 2) show that the spectra of both isomers **3** and **4** are quite distinct. The C≡N stretching wavenumbers of both phosphino species are slightly

smaller than the corresponding values of the amino analogues. The downward wavenumber shift amounts to 89 cm⁻¹ for the isocyanide chromophore upon replacement of NH₂ by PH₂ (2227 cm⁻¹ in **1** and 2138 cm⁻¹ in **3**) and to only 30 cm⁻¹ for the cyanide chromophore (2343 cm⁻¹ in **2** and 2313 cm⁻¹ in **4**). The N≡C stretching mode of **3** exhibits the strongest intensity in the H₂PNC spectrum whereas the C≡N stretching of **4** is almost inactive. This is presumably due to the changes in the local dipole moment and/or the admixture of other degrees of freedom. A quantitative analysis should be carried out before any conclusion can be drawn. The five vibrational modes related to the PH₂ groups are systematically less intense in **3** than in **4**. In addition, it is surprising that the P–N stretching vibration of **3** is associated with a larger wavenumber (637 cm⁻¹) than the P–C stretching of **4** (585 cm⁻¹). A reverse ordering has in fact been found for the N–N and C–N stretching modes in **1** and **2**, respectively, namely, with the wavenumbers of 886 and 1047 cm⁻¹ (at the same level).

Table 4 Calculated relative energies for the CH₂N₂ and CH₂PN systems^a

Method//geometry	CH ₂ N ₂ System			CH ₂ PN System		
	H ₂ N-NC (1)	H ₂ N-CN (2)	TS: (1) → (2) (5)	H ₂ P-NC (3)	H ₂ P-CN (4)	TS: (3) → (4) (6)
HF/6-31G(d)//HF/6-31G(d)	0.0	-43.6	42.6	0.0	-11.5	34.9
MP2/6-31G(d)//HF/6-31G(d)	0.0	-48.0	44.0	0.0	-19.9	27.8
MP4SDQ/6-31G(d)//HF/6-31G(d)	0.0	-44.7	40.5	0.0	-17.0	28.9
HF/6-31G(d,p)//HF/6-31G(d,p)	0.0	-44.1	42.5	0.0	-19.9	27.9
MP2/6-31G(d,p)//MP2/6-31G(d,p)	0.0	-49.1	45.3	0.0	-21.2	28.9
MP2/6-311G(d,p)//MP2/6-311G(d,p)	0.0	-47.7	44.2	0.0	-21.2	27.7
MP2/6-311++G(d,p)//MP2/6-311G(d,p)	0.0	-48.5	43.5	0.0	-20.8	27.5
MP3/6-311++G(d,p)//MP2/6-311G(d,p)	0.0	-44.4	40.7	0.0	-16.3	28.1
MP4SDQ/6-311++G(d,p)//MP2/6-311G(d,p)	0.0	-44.2	40.8	0.0	-16.4	28.9
MP4SDTQ/6-311++G(d,p)//MP2/6-311G(d,p)	0.0	-44.8	39.9	0.0	-17.9	27.6
CISD/6-311++G(d,p)//MP2/6-311G(d,p)	0.0	-44.4	41.7	0.0	-14.5	30.3
CISDQ/6-311++G(d,p)//MP2/6-311G(d,p)	0.0	-44.0	38.9	0.0	-16.4	28.0
CISDQ/6-311++G(d,p) + E _{zp} ^b	0.0	-43.9	36.9	0.0	-16.1	27.1

^a Calculated using total energies from Table 3. ^b Including zero-point energy corrections obtained at the HF/6-31G(d,p) level and scaled by 0.9.**Table 5** Total and relative energies for the CHN system^a

Method ^b	E(HNC)	Relative energies		
		H-N≡C	H-C≡N	TS: C(H)N
MP2/6-311++G(d,p)	-93.173 54	0.0	-18.6	34.2
MP3/6-311++G(d,p)	-93.178 12	0.0	-13.9	34.5
MP4SDQ/6-311++G(d,p)	-93.185 78	0.0	-14.9	33.7
MP4SDTQ/6-311++G(d,p)	-93.201 43	0.0	-16.0	33.2
CISD/6-311++G(d,p)	-93.163 63	0.0	-13.7	34.7
CISDQ/6-311++G(d,p)	-93.187 86	0.0	-14.8	32.8
MP2/6-311++G(2d,2p)	-93.193 71	0.0	-18.0	34.9
CISD/6-311++G(2d,2p)	-93.180 44	0.0	-13.5	34.9
CISDQ/6-311++G(2d,2p)	-93.206 66	0.0	-14.4	33.2
MP2/6-311++G(df,2pd)	-93.204 07	0.0	-17.7	34.3
CISD/6-311++G(df,2pd)	-93.191 57	0.0	-12.9	35.1
CISDQ/6-311++G(df,2pd)	-93.217 93	0.0	-14.0	33.0
MP2/6-311++G(2df,2pd)	-93.222 19	0.0	-17.7	35.1
CISD/6-311++G(2df,2pd)	-93.206 53	0.0	-13.1	35.5
CISDQ/6-311++G(2df,2pd)	-93.234 78	0.0	-14.2	33.7
CISDQ/6-311++G(2df,2pd) + E _{zp} ^c		0.0	-13.8	30.8
CISDQ/6-311++G(d,p) + E _{zp} ^c		0.0	-14.4	29.9
Expt. ^d		0.0	-14.8	

^a Based on MP2/6-311G(d,p) optimized geometries. HN≡C: r(CN) = 1.180 Å, r(NH) = 1.000 Å; HC≡N: r(CN) = 1.170 Å, r(CH) = 1.068 Å; transition structure for 1,2-H shift: C(H)N: r(CN) = 1.190 Å, r(CH) = 1.170 Å, α(HCN) = 74.3°. ^b Core orbitals are frozen in correlation treatments. ^c The zero-point energies (kcal mol⁻¹) are: HNC: 9.7, HCN: 10.1 and TS: 6.8. ^d Ref. 19(a).**Table 6** Atomic net charges and dipole moments of equilibrium structures calculated at the MP2/6-311G(d,p) level

		H ₂ NNC (1) (X = N)	H ₂ NCN (2) (X = N)	H ₂ PNC (3) (X = P)	H ₂ PCN (4) (X = P)
Atomic charge ^a	C	-0.07	0.40	0.00	0.00
	N	-0.09	-0.36	-0.39	-0.27
	X	-0.46	-0.67	0.46	0.31
Dipole moment/D		4.11	4.33 (4.3) ^b	3.43	3.32

^a Based on Mulliken population definitions. ^b Experimental value given in parentheses, taken from ref. 11.

Relative Energies.—We turn now to a consideration of relative energies between isocyanides and cyanides (Tables 4 and 5) to assess the thermodynamic stability of phosphinoisocyanide **3** at the Hartree-Fock level. The results for phosphino molecules **3** and **4** are more sensitive to the presence in the basis set of polarization p-functions on hydrogen with a decrease of 8 kcal mol⁻¹ in going from HF/6-31G(d) to HF/6-31G(d,p). However, this energy change has begun to be reduced at the MP2 level.

Two previous results of the energy difference between isocyanamide **1** and cyanamide **2** have been reported. Earlier SCEP/DZP calculations using HF/DZP-geometries¹⁴ reported a value of 53 kcal mol⁻¹ in favour of **2** while more recent MP4/6-311++G(d,p) calculations using HF/6-31G(d)-geometries together with E_{zp} corrections derived a value of 44.9 kcal mol⁻¹.⁷ The latter value is similar to the corresponding value obtained in the present work using MP2/6-311G(d,p)-geometries (Table 4). Our best estimate at CISDQ/6-311++

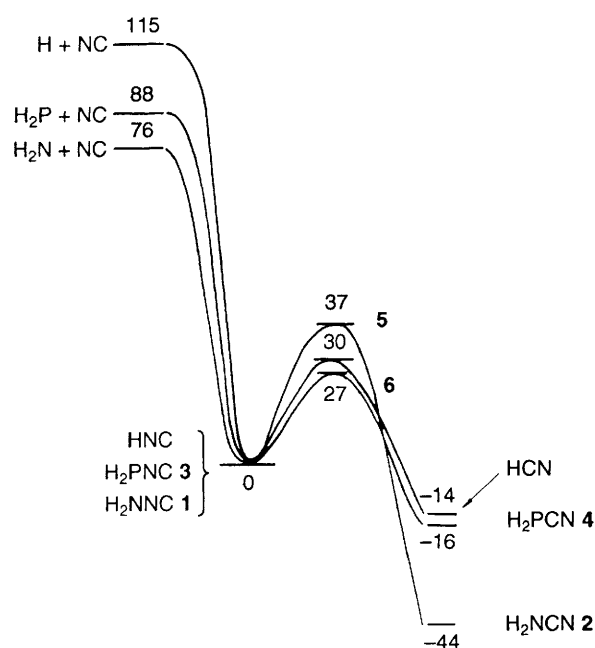


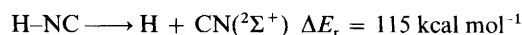
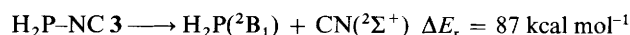
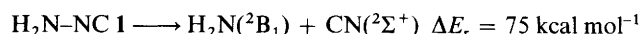
Fig. 4 Schematic potential energy profiles for the isocyanide-cyanide rearrangements and fragmentation reactions; values are given in kcal mol⁻¹ [at CISDQ/6-311++G(d,p) + E_{zp}]

G(d,p) + E_{zp} gives a value of 43.9 kcal mol⁻¹. Surprisingly, phosphinoisocyanide **3** is calculated to lie only 16.1 kcal mol⁻¹ above phosphinocyanide **4** at the same level.

The reliability of the above values can be assessed by considering the situation of the parent HNC-HCN system for which an experimental result^{19a} as well as high-level calculations^{19b} of the energy difference are available. Table 5 lists the energetic results of the CHN isomers using different types of basis set. Extension of the polarization space tends to reduce slightly the energy difference between both isomers but the situation seems to be stabilized with the 6-311++G(2df,2pd) basis. At the CISDQ level, a change of only -0.6 kcal mol⁻¹ occurs upon extension of the basis from 6-311++G(d,p) to 6-311++G(2df,2pd). The present best estimate using the CISDQ/6-311++G(2df,2pd) value and corrected for zero-point energy indicates that hydrogen isocyanide lies 13.8 kcal mol⁻¹ above hydrogen cyanide. The latter agrees well with the experimental value of 14.8 ± 2 kcal mol⁻¹ estimated from an ion-cyclotron resonance experiment^{19a} and the calculated value of 14.4 ± 1 kcal mol⁻¹ from coupled-cluster CCSD(T)-wavefunctions with a large (d,f)-basis set.^{19b} For the sake of consistency, we employed the value of 14.4 kcal mol⁻¹ obtained from CISDQ/6-311++G(d,p) + E_{zp} energies to compare with the values mentioned above for both amino and phosphino systems. It can thus be concluded that phosphinoisocyanide **3** exhibits thermodynamic stability similar to hydrogen isocyanide (HNC), relative to the corresponding cyanides. The isocyanide **3** is comparatively lower in energy than the amino analogue **1** relative to their corresponding cyanide isomers.

Fragmentation Products.—We have also considered the homolytic dissociation of both isocyanides **1** and **3** in order to gain additional information on their stability. The geometries of the NH₂, PH₂ and CN fragments were optimized using the unrestricted UMP2/6-311G(d,p) method. Because the UHF

wavefunctions of the CN radical are heavily contaminated by higher spin states, we employed a projected Møller-Plesset formalism (PUMP4)⁹ with the 6-311++G(d,p) basis set to obtain their total energies.* Together with the MP4SDTQ/6-311++G(d,p) energies of **2** and **4** given in Table 3, and of HNC in Table 5 the dissociation energies are evaluated as follows (including E_{zp}).



The phosphorus-nitrogen bond is thus stronger than the nitrogen-nitrogen bond (by about 12 kcal mol⁻¹), and contributes to the stabilization of the phosphinoisocyanide molecule **3** as compared with its amino analogue **1**.

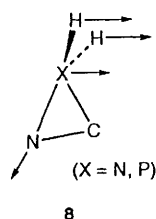
Electronic Distribution.—As seen in Table 6, the carbon atom in both phosphino molecules **3** and **4** is neutral. The phosphorus atom carries a large positive charge. Within each pair of isomers, both have similar dipole moments; the phosphino molecules overall have smaller dipole moments than the amino analogues. To gain further information on the electronic distribution, we also calculated the molecular electrostatic potentials²⁰ of the equilibrium structures. The potential maps are displayed in Fig. 3. As expected, the lone-pair electrons of the terminal nitrogen atoms in cyanides exhibit a deeper electrostatic potential than those of the carbons in isocyanides. In general, the potential minima of the phosphino isomers **3** and **4** lie in between those of the parent HNC-HCN molecules and the amino **1** and **2**. The latter present the deepest electrostatic potential minima. These results suggest that a similar ordering of the proton affinities within each of the two analogous series could be observed.

1,2-Rearrangement Reactions.—We have considered both transition structures **5** and **6** for the 1,2-sigmatropic shifts of the amino and phosphino groups, respectively, around the C≡N group (Fig. 1). The relevant optimized geometries are listed in Table 1 and energetic results calculated at a number of levels are recorded in Tables 3 and 4. Energetics of the transition structure connecting the parent HNC-HCN system are listed in Table 5.

The geometry of the transition structure **5** has previously been optimized at the HF/DZP level.¹⁴ It is surprising to note that these parameters are only qualitatively comparable to the HF/6-31G(d,p) results obtained in the present work. However, our calculations concur with the earlier study¹⁴ which points out that (i) in **5**, the amino group is pyramidalized toward the carbon atom rather than the nitrogen, and (ii) within the three-membered bridge, the C-N distance is much shorter than the N-N¹ distance (Table 1). With regard to the motion of the nuclei along the reaction path, the C-N¹ group moves in two opposite directions, depending on the identity of the reactant, to reach the transition structure **5**. Starting from the cyanide **2**, the NCN moiety bends while maintaining and keeping the existing *trans*-configuration around the N-C distance. In contrast, starting from the isocyanide **1**, the NNC moiety has to bend to form a *cis*-configuration as seen in structure **5**. Thus, it seems paradoxical that the transition structure **5** is structurally closer to the cyanide **2** which is the more stable of the two minima under consideration. This behaviour is rather general, because a similar situation can again be found in the transition structure **6** connecting both phosphino isomers **3** and **4** (Table 1). The P-C distance in **6** is 0.12 Å shorter than the P-N. Similarly the transition structure of the CHN system has a shorter C-H distance (1.170 Å) than the N-H (1.425 Å). Nevertheless, if we

* The UMP2/6-311G(d,p)-geometries are: CN(²Σ⁺): $r = 1.129$ Å; NH₂(²B₁): $r = 1.025$ Å, $a = 102.1^\circ$; PH₂(²B₁): $r = 1.412$ Å, $a = 92.2^\circ$. The PUMP4SDTQ/6-311++G(d,p) energies (hartree) are: CN: -92.509 36; NH₂: -55.759 17 and PH₂: -342.010 73.

consider the ratio between the distances in the transition structure and the corresponding minima, we find that both ratios $r_{\text{PN}}(6)/r_{\text{PN}}(3)$ and $r_{\text{PC}}(6)/r_{\text{PC}}(4)$ of the phosphino species are about the same (1.2), whereas in the amino species, **1**, **2** and **5**, the ratio of distances to carbon $r_{\text{NC}}(5)/r_{\text{NC}}(1)$ is much favoured over that to nitrogen [$r_{\text{NN}}(5)/r_{\text{NN}}(2)$ (1.2 *versus* 1.4)]. Such a difference is presumably due to the relative strength of the different bonds involved in the sigmatropic shift. Because the C–N bond is stronger than the N–N, a significant stabilization can be gained in the transition structure **5** by retaining (if starting from H_2NCN), or by forming preferentially (if starting from H_2NNC) a partial bond to carbon.



The transition vector of both transition structures **5** and **6** is sketched in **8**. The imaginary wavenumbers associated with this reaction mode amount to $636i$ and $463i$ cm^{-1} in **5** and **6**, respectively [at HF/6-31G(d,p)].

Our calculations predict energy barriers of 36.9 and 27.1 kcal mol^{-1} for the unimolecular conversions of isocyanamide **1** and phosphinoisocyanide **3**, respectively, to the corresponding cyanides (Table 4). The latter is compared to the barrier of 29.9 kcal mol^{-1} , calculated using the same level, for the $\text{HNC} \rightarrow \text{HCN}$ conversion (Table 5).

Results listed in Table 5 also point out that extension of the basis set only marginally modifies the energy barrier [30.8 kcal mol^{-1} using the large 6-311++G(2df,2pd) basis]. The latter compares well with the value of 30.2 kcal mol^{-1} recently obtained using coupled-cluster CCSD(T) calculations with a comparable basis set.^{19b} This good agreement again lends confidence to our predicted energy barriers for the N and P analogues. We would estimate an uncertainty of about ± 2 kcal mol^{-1} on our predicted relative energies.

Fig. 4 indicates that although isocyanamide **1** is the least thermodynamically stable species, it presents the largest kinetic stability amongst three isocyanides examined. Phosphinoisocyanide **3** is somewhat kinetically less stable than hydrogen isocyanide with regard to unimolecular rearrangement, but it should also be observable in both gaseous or low-temperature condensed phases.

Proceeding in the opposite direction, from cyanide to isocyanide, both molecules H_2PCN **4** and HCN require a similar activation barrier for rearrangement (43–44 kcal mol^{-1}) while the H_2NCN molecule requires a substantial energy (about twice as large, 81 kcal mol^{-1}).

Conclusions

In this paper, we have presented a detailed theoretical study of the isocyanide–cyanide rearrangement involving H, H_2N and H_2P as the migrating groups. Structures and properties of the equilibrium structures have also been determined. Phosphinoisocyanide is found to lie about 16 ± 2 kcal mol^{-1} above phosphinocyanide and to rearrange to the latter with an energy barrier of about 27 ± 2 kcal mol^{-1} . Thus, phosphinoisocyanide possesses a thermodynamic and kinetic stability

similar to hydrogen isocyanide with respect to the corresponding cyanides. Aminoisocyanide (isocyanamide) has a lesser thermodynamic stability (44 kcal mol^{-1} above cyanamide) but a larger kinetic stability (an energy barrier of 39 kcal mol^{-1}). Overall these data suggest that phosphinoisocyanide could be detected spectrometrically in both gaseous and condensed phases. Phosphinoisocyanides substituted by bulkier and more stabilizing groups could thus be considered as synthetic targets and employed for further studies of the reactivity of the isocyanide functional group.

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