

$F_2P\equiv N$: A Remarkably Stable Species

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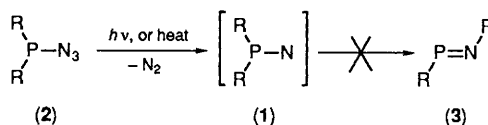
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Ab initio MO calculations show that F_2PN is remarkably stable, lying about 70 kJ mol^{-1} lower in energy than its conventional valence isomer difluoro-iminophosphane ($FP=NF$) and could thus be a candidate for an actual synthesis in the laboratory.

It is now recognized that nitrenes (**1**) are formed as transient intermediates during the thermolysis or photolysis of phosphinoazides (**2**).¹ In these reactions, no Curtius-type rearrangement leading to iminophosphanes (**3**) was observed (Scheme 1). Intermediates (**1**) have been shown to undergo 1,2-addition reactions with trapping agents or polymerisation rather than typical insertion reactions of nitrenes.^{1,2}

The presence of a lone pair of electrons on the phosphorus atom seems to stabilize markedly the nitrene singlet state with respect to its conventional isomer and thus to enlarge the barrier height that in turn inhibits the unimolecular rearrangement (**1**) \rightarrow (**3**). Nevertheless, no spectroscopic evidence for the existence of (**1**) has been obtained yet. This may be due to the inherent instability of nitrenes. Earlier MO calculations³ showed that the singlet phosphinonitrene (H_2PN , singlet

ground state) lies in fact about 167 kJ mol^{-1} higher in energy than iminophosphane ($HP=NH$). In this context, we have been interested in searching for substituents that could stabilise the nitrene form (**1**) [relative to (**3**)] through a strong electronic effect. In the present communication, we report the results of *ab initio* MO calculations showing that the fluorine atoms exert a dramatic effect on the relative stability between the isomers (**1**) and (**3**).

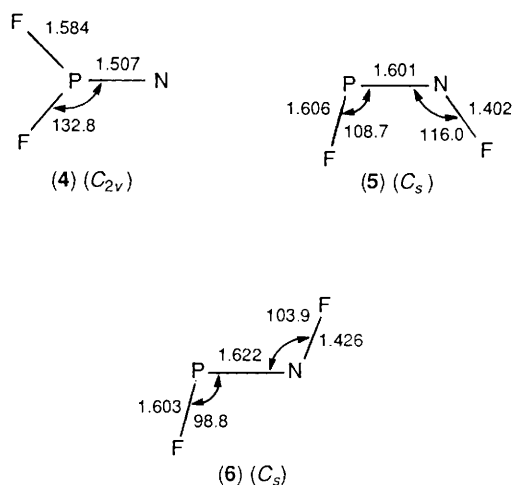


Scheme 1

Table 1. Total (Hartree) and relative (kJ mol⁻¹) energies for F₂PN species.

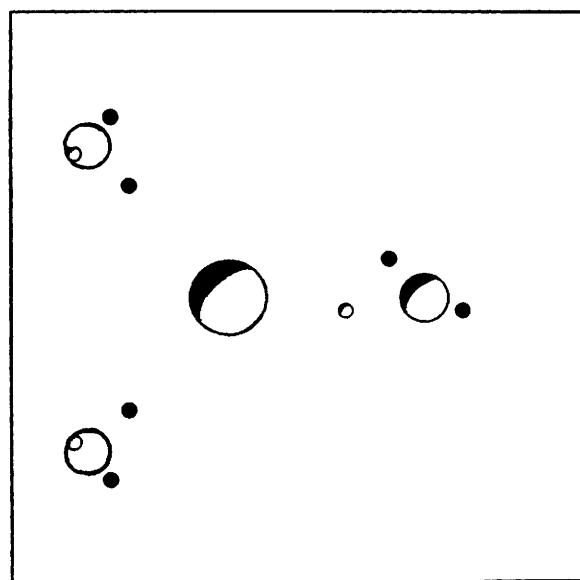
Level ^a	Basis set	Total energy			Relative energy	
		Nitrene (4)	<i>cis</i> -(5)	<i>trans</i> -(6)	$\Delta E(5) - (4)$	$\Delta E(6) - (5)$
HF	6-31G*	-593.97113	-593.94293	-593.93995	74	8
MP2(F) ^b	6-31G*	-594.63667	-594.58960	-594.58750	124	5
MP3(F) ^b	6-31G*	-594.61900	-594.58790	-594.58614	82	5
MP4SDTQ(F) ^b	6-31G*	-594.66838	-594.62879	-594.62741	104	4
CISD ^c	6-31G*	-594.52808	-594.49540	-594.49299	86	6
CISDQ ^d	6-31G*	-594.61556	-594.58324	-594.58157	85	4
HF	6-31+G* ^e	-593.98386	-593.95721	-593.95391	70	9
MP2	6-31+G* ^e	-594.66521	-594.62141	-594.61904	115	6
HF	6-311G*	-594.04847	-594.02673	-594.02242	57	11
MP2	6-311G*	-594.77054	-594.72964	-594.72504	109	10
MP3	6-311G*	-594.74774	-594.72415	-594.72075	62	9
CISD ^c	6-311G*	-594.67028	-594.64371	-594.63955	70	11
CISDQ ^d	6-311G*	-594.76340	-594.73691	-594.73339	70	9

^a Based on MP2/6-31G*-geometries given in Figure 1. ^b MP n (F) indicates the use of full sets of MOs. Otherwise, the 8 core orbitals are frozen in MP and CI calculations. ^c Configuration interaction calculations including all single and double substitutions. ^d The quadruple contributions are estimated by the Pople's correction. ^e Including a set of diffuse sp-functions.

**Figure 1.** MP2/6-31G* optimized geometries for the F₂PN species considered. Bond lengths given in Å and bond angles in degrees.

We have considered three fluoro-substituted species (F₂PN): the nitrene form (4) and both the *cis*-(5) and *trans*-(6) forms of iminophosphane (Figure 1). Their geometrical parameters have been optimized at both the Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) levels using the 6-31G* basis set.⁴ Harmonic vibrational frequencies calculated at the HF/6-31G* level show that all three structures (4), (5), and (6) are local minima. Relative energies between them are determined employing different levels of accuracy⁴ with MP2/6-31G*-optimized geometries. Calculated results are summarized in Figure 1 and Table 1.

Of the two geometrical isomers (5) and (6), the *cis*-form (5) is calculated to be lower in energy (Table 1). Improvement of the basis set marginally increases the energy difference between the *cis*- and *trans*-isomer. According to our best value obtained from CISDQ/6-311G* calculations, the *cis*-iminophosphane (5) lies 9 kJ mol⁻¹ below *trans*-(6). This energy ordering is similar to that of the isovalent system FN=NF⁵ in which a *cis*-effect⁶ of the two fluorine atoms also favours the *cis*-FN=NF isomer, essentially due to the n(F¹)-σ*(F²) interaction.

**Figure 2.** Localized orbital charge centroids in the F₂PN species (4). ● are centroids in the molecular plane. ○ indicate two symmetrical centroids situated above and below the molecular plane.

The most important conclusion supported by the results in Table 1 is that the *cis*-iminophosphane (5) turns out to be higher in energy than its valence isomer (4). Such behaviour is quite remarkable compared with the unsubstituted (H₂PN) species mentioned above. It clearly emphasises a surprisingly strong electronic effect exerted by the F-atoms in stabilizing the nitrene moiety through a P-centre. We note that our best calculations at the CISDQ/6-311G* level predict a value of 70 kJ mol⁻¹ for the energy difference between the fluoro-substituted iminophosphane and phosphinitrene isomers. Incidentally, the rather poor convergence of the MP expansion (Table 1) indicates that higher-order correlation energy terms should certainly be included in order to make a more reliable prediction for the relevant energy differences. In any case, it is likely that the qualitative energy ordering between species (4) and (5) will remain unchanged at all levels of approximation.

All three species considered are calculated to be planar. The calculated P-F and P-N bond distances in phosphinonitrene (**4**) are both shorter than in the corresponding iminophosphane (**5**), particularly for the P-N bond (by 0.1 Å, Figure 1). The P-N distance of 1.507 Å in (**4**) is slightly shorter than that of 1.515 Å previously found for H₂PN⁷ (at MP2/6-31G**). An orbital localization according to Boys' method⁸ with the 6-31G* basis set shows that three charge centroids of localized orbitals are centred in the region between the P and N atoms (Figure 2). Two of the centroids are symmetrical with respect to the molecular plane and quasi equidistant to P and N. The third centroid is in the molecular plane and closer to the N atom. The fluorine atoms induce the migration of a nitrogen lone pair into the P-N bonding region. This fact supports the view that the phosphorus-nitrogen bond in (**4**) can better be described as a classical dative triple bond (F₂P≡N).

Because of its remarkable stability, the nitrene (**4**) constitutes an attractive candidate for a preparation in the laboratory. Thus, the question of interest is: how might this nitrene be prepared? Because the phosphinoazide F₂PN₃ is expected to be explosive (*cf.* Scheme 1), one seemingly reasonable alternative could be the use of the phosphino isocyanate (F₂P-N=C=O) as a starting material. For instance, Maier and co-workers⁹ have recently been successful in isolating aminonitrene (H₂NN) from a photolysis of amino isocyanate (H₂N-N=C=O) in an argon matrix at 12 K.

In summary, the present theoretical study suggests that F₂PN is a remarkably stable species. It is probably more reasonable to classify this molecule as an F₂P≡N phosphonitrile than as a phosphinonitrene. A detailed analysis of the effect of F-atoms on the bonding phenomenon as well as a detailed comparison of the electronic structure of F₂P≡N and

FP=NF with the isovalent F₂N₂ and F₂P₂ systems will be reported in a forthcoming publication. We hope that the present communications will stimulate an experimental search for this unusual and interesting species.

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