Phosphoric–Carboxylic Imides. Part 4. MNDO Molecular Orbital Calculations on *N*-Formylphosphinamide, $H_2P(O)NHCHO$, and Related Systems

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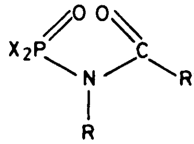
MNDO molecular orbital calculations were carried out on the mixed imide $H_2P(O)NHC(O)H$ (1), its conjugate base $H_2P(O)NC(O)H^-$ (1a), and the product of its rearrangement, $H_2P(O)OC(NH)H$ (2), using optimised geometries. The molecular parameters obtained for (1) are in good agreement with those determined for two mixed phosphoric–carboxylic imides by *X*-ray diffraction. Comparison of (1) and (1a) shows that deprotonation affects mainly the NC(O) fragment. Calculations show that (1) should be more stable than the isomer (2), and that their interconversion should be of a concerted nature.

We have recently found that the mixed imide system (A) represents an attractive model for structural and reactivity studies. The structural [1] and spectroscopic data,[2] as well as the fragmentation,[3] solvolytic,[4] and nucleophilic [5] behaviour of (A) indicate that the carbonyl oxygen represents the most nucleophilic and the phosphorus atom the most electrophilic centre of the molecule. This pattern of electronic distribution is responsible for both the reactivity and the structural characteristics of (A), the latter including conformational preferences, bond distances and angles, and intramolecular interactions.

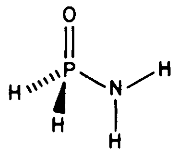
In view of the recently accumulated data on the chemistry of (A), we decided to carry out molecular orbital calculations on the molecule $H_2P(O)NHC(O)H$ (1) [*i.e.* (A; X = R = R′ = H)], its conjugate base $H_2P(O)NC(O)H^-$ (1a), and the isomeric rearrangement product $H_2P(O)OC(NH)H$ (2), in order to correlate calculated results with the available experimental data. Our MO calculations were carried out at the semi-empirical MNDO level.[6,7] However, the existing version of MNDO is parameterised for trivalent phosphorus, and the results of calculations on molecules containing phosphorus in its expanded valence state should be viewed with caution.[8] In order to test the applicability of the MNDO programme to systems such as (A), we have determined the optimised geometries and energies of the two conformations (3a) and (3b) of the model phosphinamide $H_2P(O)NH_2$ and have compared these results with those previously obtained [9] from *ab initio* calculations (Table 1).

Like STO-3G, MNDO predicts (3b) to be marginally more stable than (3a). Although other geometrical properties were in close agreement, the MNDO-derived P=O bond lengths (*ca.* 1.5 Å) are much closer to experimental [1.47 Å for $Ph_2P(O)NMe_2$[10]] than are the *ab initio*-derived values (*ca.* 1.6 Å[9]). Encouraged by these results, we have determined the MNDO energies and optimised geometries for the model system (1), its conjugate base (1a), and its rearrangement product (2).

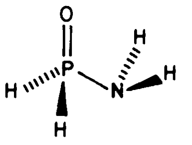


(A)

$H_2P(O)NHC(O)H$ (1)
$H_2P(O)NC(O)H^-$ (1a)
$H_2P(O)OC(NH)H$ (2)



(3a)



(3b)

Results and Discussion

The calculated energies of the optimised planar geometries for all four possible conformations of (1) are as shown in the Scheme. The lowest energy conformation is the *Z,E*-structure, which can be directly compared with the conformations of dimethyl *N*-benzoylphosphoramidate (4) [1] and 2-formylamino-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (5),[11] as determined by *X*-ray diffraction. This comparison is presented in Figure 1.

The calculations not only indicate the greatest stability of the *Z,E*-conformation, which corresponds to that observed in the solid state, but also yield molecular parameters for (1) that are in good agreement with the experimental values obtained for compounds (4) and (5). In (4) the OPNCO fragment is also virtually planar;† the only deviation from planarity of the molecule involves the phenyl group, with the benzene ring twisted out of plane as a result of the steric requirements of the *ortho*-hydrogen atoms. It is important to note that the calculations also indicate a close contact (3.05 Å) between the nucleophilic carbonyl oxygen and electrophilic phosphorus of (1) which we previously interpreted for (4) (2.97 Å) as an 'early stage' of the formation of a P^V tbp (trigonal bipyramidal) intermediate.

The optimised geometry of the isomeric formimidate derivative (2) [formed by phosphoryl transfer in (1) from N to O] is given in Figure 2. Interestingly enough, the P···N distance in (2) (2.93 Å) is also smaller than the sum of the van der Waals radii (3.4 Å). The *E*-form of (2) shown in Figure 2 is more stable than the *Z*-form by *ca.* 9 kcal mol^{-1}; nevertheless even this most stable conformation of (2) (ΔH_f 32.33 kcal mol^{-1}) is *ca.* 13 kcal mol^{-1} less stable than the parent structure (1). This result implies that mixed imides of the type (1) should be stable and should not exhibit a tendency to rearrange to system (2). In agreement with this conclusion, we have never observed any spontaneous rearrangement of

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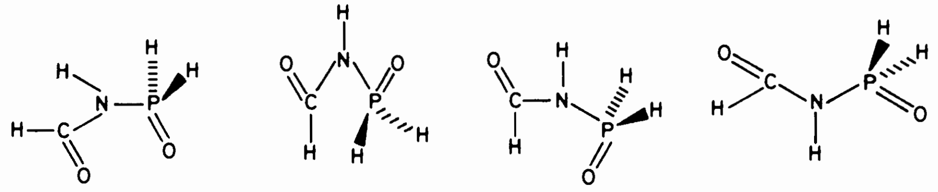
† No data on the planarity of the OPNCO group in (5) are given in ref. 11.

Table 1. MNDO geometries for (3a) and (3b) (STO-3G results [9] in parentheses)

Structure	PO	PN	PH	NH	$\widehat{OPN}$	$\widehat{OPH}$	$\widehat{PNH}$	ΔH_f/kcal mol^{-1}
(3a)	1.499 (1.59)	1.636 (1.69)	1.37 (1.4)	0.99 (1.01) 0.988	111.8 (108.0)	115.8 (117.0)	122.5 (122.0) 121.5	−3.92 ΔE 4.335 (6.9)
(3b)	1.50 (1.62)	1.689 (1.75)	1.366 (1.39)	1.00 (1.02) 1.00	113.9 (114.0)	115.1 (117.0)	110.7 (111.0) 110.7	−8.255



Conformation	Z,Z	E,E	E,Z	Z,E
ΔH_f (kcal mol^{-1})	−39.1	−42.2	−42.7	−45.2

Scheme.

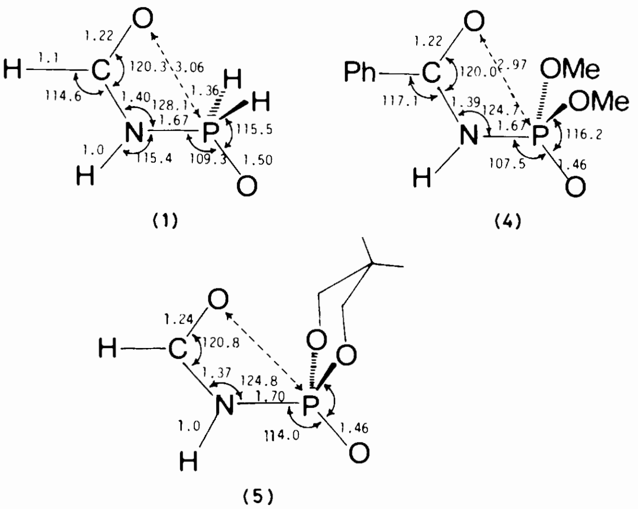

(1) (4) (5)

Figure 1. The lowest energy conformation of (1) and the molecular parameters of (4) and (5)

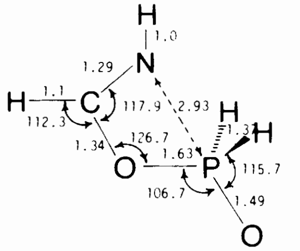
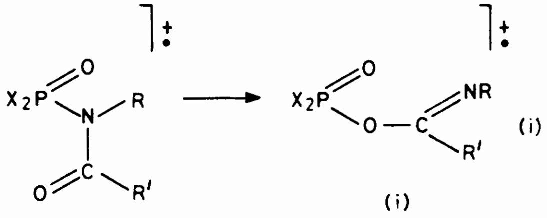

(2)

Figure 2. The optimised geometry of (2)


(i)

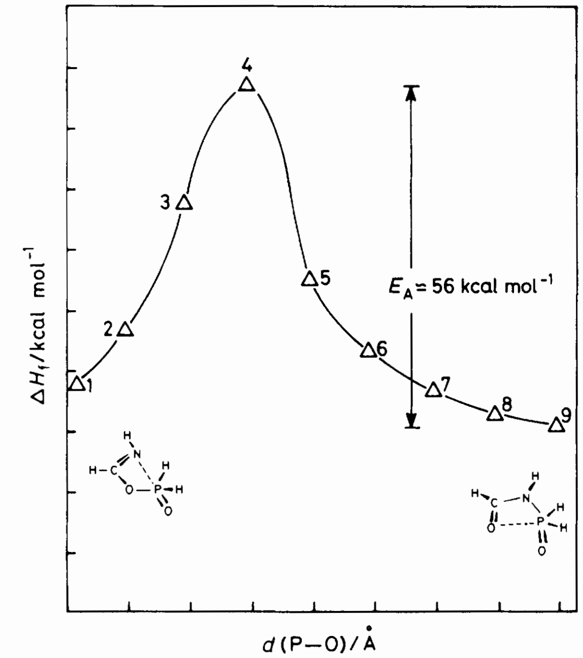
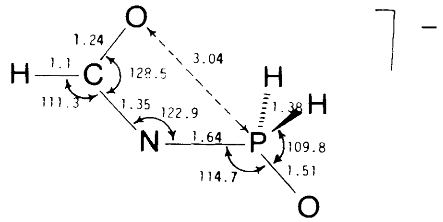


Figure 3. Energy *vs.* P–O distance plot for (1) ⇌ (2) rearrangement

synthesized structures (1) to (2). However, we have demonstrated that N ⟶ O phosphoryl migration [equation (i)] does occur under electron-impact conditions.[3]

Since both model structures (1) and (2) are planar, we have optimised the geometry/energy for several P–O bond distances starting from the formimidate molecule (2) (Figure 3). Clearly, shortening of the P–N distance is concomitant with P–O extension to yield finally the mixed imide (1), *i.e.* con-



(1a)

Figure 4. The optimised geometry of (1a)

Table 2. π-Bond order of the mixed imide group

Bond	(1)	(1a)
O-C	0.86	0.74
C-N	0.43	0.61
N-P	0.20	0.26
P-O	0.38	0.40

certed rearrangement occurs with E_a *ca.* 56 kcal mol^{-1}. The geometry at point 8 is virtually identical with that of one (*Z*,*Z*) of the fully optimised conformations of (1). The calculations therefore predict that the imide structure (1) should be stable but could undergo a concerted endothermic rearrangement at higher temperatures. With respect to the concerted nature of the (2) $\longrightarrow$ (1) rearrangement mechanism, it is of interest that recent MNDO SCF-MO calculations have suggested that the analogous *O*-acyl imidate $\longrightarrow$ imide isomerisation is similarly concerted, proceeding with synchronous C-N bond formation and C-O bond cleavage.[12]

Secondary phosphoric-carboxylic imides can be easily converted into their conjugate bases upon treatment with strong base (NaH, Na, *etc.*) [equation (ii), R = H].

$$X_2P(O)\text{-}NH\text{-}C(O)R \xrightarrow{\text{base}} [X_2P(O)\text{-}N\text{-}C(O)R]^- \quad \text{(ii)}$$

The geometry of the fully optimised anionic form of the model imide (1a) is presented in Figure 4. Comparison of structures (1) and (1a) shows that deprotonation of (1) has a greater effect upon the bonding at the carboxamide rather than at the phosphoramide fragment of the molecule. This can best be illustrated by comparing the calculated π-bond orders within the OCNPO framework of the neutral molecule (1) and its conjugate base (1a) (Table 2). We have also calculated the net atomic charges of all atoms in (1) and (1a); the values obtained are listed in Table 3. It is interesting that the net charge at phosphorus changes negligibly with deprotonation of the molecule. This result is in excellent agreement with earlier MO calculations indicating that the charge on phosphorus is not sensitive to changes in its bonding environment.[13] Although the net atomic charges indicate highest electron density at the phosphoryl oxygen, the greatest *increase* in negative charge upon deprotonation occurs at the carbonyl oxygen. It should also be noted that the additional electron of the anion (1a) resides in a HOMO which has π character with $2p_z$ coefficients of 0.775, 0.084, and -0.524 on N, (P)O, and (C)O, respectively. This suggests that where HOMO-LUMO interactions are important, the reaction would involve the nitrogen or the carbonyl oxygen rather than the phosphoryl oxygen.[14] This observation is relevant to the nucleophilic behaviour of systems (A) and their conjugate bases. Our experiments on the alkylation of the conjugate base of (4)[5] showed that, depending on the reaction conditions, alkylation takes place either predominantly or exclusively at the carbonyl oxygen atom. For other mixed imide systems (A), alkylation at the nitrogen atom has been reported.[15] It is therefore clear that the anion (2) can behave as an ambident (but mainly NCO) nucleophile, and that small variations in reaction conditions, particularly in terms of steric interactions in the nucleophile-electrophile transition state can change the intramolecular selectivity in substitution reactions.

Table 3. Net atomic charges in (1) and (1a)

	Charge (*e*)	
Atom	(1)	(1a)
N	-0.57	-0.62
P	0.97	0.94
(P)O	-0.61	-0.71
(P)H	-0.04	-0.19
(P)H	-0.04	-0.19
(N)H	0.20	
C	0.38	0.31
(C)O	-0.35	-0.53
(C)H	0.07	0.00

Calculations

The calculations were performed on a Burroughs 6 800 computer using the QCPE version of MNDO by W. Thiel.[16] In computing the lowest energy conformations of *N*-formylphosphinamide (1), its anion (1a), the phosphinamide (3), and the formimidate (2), full energy and geometry optimisation was employed. Higher energy conformations of (1), (2), and (3) were frozen into the molecules by fixing the appropriate torsion angles, all other geometrical variables being optimised. In the study along the reaction co-ordinate for the formimidate (2)-*N*-formylphosphinamide (1) transformation, all atoms except (P)H_2 were held in a planar arrangement while bond angles and bond lengths were optimised at each increment in the P-O bond length. The initial input for geometrical parameters for (1) was taken from the crystal structure of (4);[1] that for (3) was taken from *ab initio* calculations on the same molecule.[9] In addition a generally accepted[17] bond length of 1.42 ± 0.02 Å was used for P-H bonds.

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