(27) Taking the radius of a DHP vesicle to be 250 Å and the bilayer thickness to be 50 Å, we calculate that each vesicle contains 18 000 surfactant molecules and has external and internal areas of 7.85 × 10^5 and 5.02 × 10^5 Å^2, respectively. At the preparations used ([DHP] = 2.28 × 10^{-3} M), the vesicle concentration is 1.24 × 10^{-7} M. Thus, each vesicle contains ~800 pyrene molecules.

(28) The stoichiometric concentration of benzophenone varied between 3 and 10 × 10^{-6} M^{-1}. Benzophenone distributes itself, of course, between the bulk solvent and the surface of the vesicle. The average decrease between pyrene and benzophenone is rather small since, on the time scale of our observation (2 ns), we could not see the buildup of the transient absorption at 610 nm (owing to the benzophenone anionic radical).

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(30) At laser intensities of 50–150 mJ per pulse (~50- to 70-fold higher intensities than those used in the present work), photoionization of pyrene in anionic micellar sodium dodecyl sulfate was shown to be biphotonic.[31] The observed monophotonic ionization of 3-aminoperylene[7] was suggested to be the consequence of an apparent change in the order of photoionization from biphotonic to monophotonic as a result of decrease of charge recombination caused by the micelle.[31]

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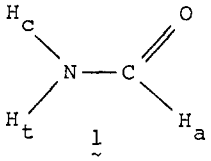
Is Formamide Planar or Nonplanar?

Sir:

The structure of formamide (NH_2CHO, **1**) is of fundamental importance in organic chemistry, particularly as a prototype for polypeptides; surprisingly, it has remained unresolved over many years. Indeed, three microwave spectral investigations over the past 20 years have led to alternating views on the planarity or nonplanarity of this molecule.[1-4] In the first of these studies in 1957, a planar structure was assumed,[1] but a subsequent study[2] in 1960 favored a nonplanar structure. This latter was (and continues to be) widely accepted.[5] It was not seriously challenged until 1974 when a redetermination[3] of the microwave spectrum returned to an interpretation in terms of a planar structure. In this communication, we use ab initio molecular orbital calculations to show that formamide lies in a very flat potential well in the vicinity of a planar structure.



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There have been numerous previous ab initio studies of formamide. Most of these have used a fixed (experimental or model) geometry[5-7] or have carried out optimizations on a structure assumed to be planar.[8] As far as we are aware, the only calculation[9] which included extensive geometry optimization and allowed for nonplanarity utilized a minimal basis set which, as we shall see, is not really adequate for situations of this type. On the other hand, it is encouraging to note that the structure and inversion barrier in ammonia itself have been shown to be well described within the Hartree–Fock approximation.[10,11] As NH_2CHO is a formyl-substituted ammonia molecule, it seems reasonable to expect that the inversion process in formamide might be similarly well described. Our strategy here has been to carry out self-consistent-field calculations[12-14] on formamide with full-geometry optimization at increasing levels of sophistication in the basis set. We use, as a measure of the significance of the individual formamide calculations, the performance of the same basis set for ammonia where the experimental situation is more clearly defined.[15,16] Optimized structural and energy data are presented in Tables I (NH_3) and II (NH_2CHO).

We note the following points. (1) Our initial optimizations with the minimal STO-3G basis set[17] yielded a nonplanar structure (Table II) for formamide. The STO-3G basis is, however, known to underestimate valence angles at heteroatoms and, in particular, for ammonia[18] this leads (Table I) to an underestimation of the HNH angles and an inversion barrier that is too high. For this reason, STO-3G would be expected to exaggerate the degree of nonplanarity in a molecule

Table I. Optimized Structural and Energy Data for Pyramidal (C_{3v}) and Planar (D_{3h}) Forms of Ammonia^{a}

	STO-3G^{b}	4-31G^{c}	4-31G/BF	DZ + d	DZP	HF^{d}	exptl^{e}
r(N—H) (C_{3v})	1.033	0.991	1.002	1.003	1.000	0.999	1.012
∠HNH (C_{3v})	104.2	115.8	109.8	107.3	108.1	107.7	106.7
r(N—H) (D_{3h})	1.006	0.986	0.988	0.991	0.987	0.984	
E (C_{3v})	−55.45542	−56.10669	−56.12892	−56.19972	−56.20991	−56.22333	
E (D_{3h})	−55.43767	−56.10600	−56.12398	−56.18958	−56.20200	−56.21504	
barrier	11.1	0.4	3.1	6.4	5.0	5.2	5.8

^{a} Bond lengths are given in Ångstroms, bond angles in degrees, total energies in hartrees, relative energies (barriers) in kcal mol^{-1}. ^{b} From ref 18. ^{c} From ref 19. ^{d} Near Hartree–Fock results from ref 10c. ^{e} From ref 15 and 16.

Table II. Optimized Structural and Energy Data for Formamide^{a}

	STO-3G	4-31G	4-31G/BF	DZ + d^{b}	DZ + d^{c,d}	exptl^{e}
r(N—C)	1.436	1.346	1.346	1.355	1.358	1.352 ± 0.012
r(C=O)	1.216	1.216	1.191	1.197	(1.197)	1.219 ± 0.012
r(N—H$_c$)	1.027	0.993	0.995	0.996	(0.996)	1.002 ± 0.003
r(N—H$_t$)	1.026	0.990	0.991	0.994	(0.994)	1.002 ± 0.003
r(C—H$_a$)	1.104	1.081	1.091	1.089	(1.089)	1.098 ± 0.010
∠H$_c$NC	111.6	119.5	119.4	119.3	118.3	118.5 ± 0.5
∠H$_t$NC	112.1	121.9	121.7	121.5	120.4	120.0 ± 0.5
∠NCO	123.9	124.7	125.0	124.8	(124.8)	124.7 ± 0.3
∠NCH$_a$	111.9	113.7	113.7	112.8	112.8	112.7 ± 2.0
∠H$_c$NCO	21.5	0	0	0	9.1	0
∠H$_t$NCO	145.1	180	180	180	168.8	180
∠H$_a$CNO	176.6	180	180	180	178.7	180
energy	−166.69184	−168.68159	−168.75398	−168.96554	−168.96558	

^{a} Bond lengths in Ångstroms, bond angles in degrees, total energies in hartrees. ^{b} Planar structure. ^{c} Nonplanar structure. ^{d} Values in parentheses not reoptimized for nonplanar structure. ^{e} From ref 3.

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such as formamide, and an STO-3G prediction of a *nonplanar* structure is inconclusive. (2) The split-valence 4-31G basis set[19] predicts a planar structure for formamide. This basis set, however, characteristically overestimates valence angles at heteroatoms and consequently underestimates the inversion barrier in ammonia[19] (Table I). Thus 4-31G would be expected to overestimate the tendency of a molecule such as formamide to be planar and consequently the 4-31G prediction of a *planar* formamide structure is inconclusive. (3) Addition of bond functions to the 4-31G basis set (4-31G/BF) has been found[20] to lead to a significant improvement in geometric predictions, particularly for bond angles. In the case of ammonia, however, the HNH angles are still too high at 109.8° and the inversion barrier of 3.1 kcal mol^{-1} is still too low. Although the 4-31G/BF prediction of a planar formamide molecule is more meaningful than the 4-31G result, the possibility of a slightly nonplanar structure cannot be ruled out. (4) Our basis set which performs best for ammonia involves the addition of a set of d functions to a double-ζ basis set.[21-23] This double-ζ plus d-polarization basis set (DZ + d) yields, for ammonia, an HNH angle only 0.6° greater than the experimental value and an inversion barrier slightly higher (by 0.6 kcal mol^{-1}) than that observed. This gives us confidence in the use of this basis set to describe the inversion process in formamide. The optimized DZ + d structural parameters for planar formamide are in reasonable agreement with those reported in the recent microwave study[3] (cf. Table II). Distortions from the planar structure involving optimization of the 7 most important of the 12 independent geometric parameters in a completely unconstrained formamide molecule yielded a structure in which H_c, H_t, and H_a are bent 9.1, 11.2, and 1.3°, respectively, out of the NCO plane. Remarkably, this structure is lower in energy than the planar structure by only 0.03 kcal mol^{-1}. (5) If the DZ + d basis set is augmented by p functions on the hydrogen atoms,[24] yielding a full double-ζ plus polarization (DZP) basis set, results for ammonia are in somewhat poorer agreement with experiment than are the DZ + d values. In particular, the HNH angle is 1.4° too high and the inversion barrier 0.8 kcal mol^{-1} too low. This suggests that the DZ + d calculations may provide a more reliable means of studying the inversion process in formamide. Nevertheless, it is interesting to note that when the DZP basis set is applied to the DZ + d optimized structures of planar and nonplanar formamide, the former turns out to have lower energy but by only 0.04 kcal mol^{-1}. (6) Our calculations therefore suggest that formamide lies in a potential well which is very flat with respect to inversion at nitrogen in the vicinity of a planar structure.

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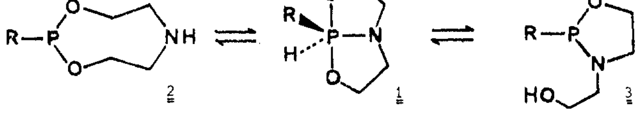
Bicyclic Phosphoranes as Precursors of Mono- or Bidentate Eight-Membered Cyclic Ligands. Coordination Compounds with the Metal in a Cradle

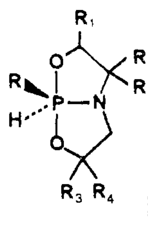
Sir:

Bicyclic phosphoranes of type **1** are structurally adapted to be in tautomeric equilibrium with open forms such as structures **2** and **3**, in which the phosphorus atom is in valence state 3. The nitrogen atom is planar in structure **1**, but becomes pyramidal in structures **2** and **3**, and would be expected to recover its donor properties. On the other hand, tautomers **2** and **3** have never been detected spectroscopically.[1]



We now report that, through the action of various atoms or cations, the bicyclophosphoranes can be converted into coordination adducts of *tautomer* **2**. The cyclic phosphorus–nitrogen ligands (L) thus unmasked behave as either monodentate or bidentate ligands. In the compounds obtained so far, the metal is *always* coordinated to phosphorus, while the coordination to nitrogen and the ligand to metal ratio depend on the reactants and experimental conditions.

When *equimolar amounts* of $M(CO)_6$ (M = Mo or W) and **1d** were allowed to react, the *monocoordinated* adducts,



1

$R = C_6H_5$

1a $R_1 = R_2 = R_3 = R_4 = H$

1b $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

(3 diastereoisomers)

1c $R_2 = CH_3$; $R_1 = R_3 = R_4 = H$

1d $R_2 = R_3 = R_4 = CH_3$; $R_1 = H$

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