ular models based on the X-ray results indicates considerable steric hindrance to reorganization. As can be seen from Figure 1, in the square pyramid (**1**) the diphosphine ethylene bridges are directed toward the Co–Cl bond, whereas they are directed away from this bond in the trigonal bipyramid (**2**). Reorganization of **1** to **2** would involve large conformational changes in the ethylene bridge, with concomitant interactions of the phenyl rings.

In addition to being the first accurate X-ray structure determinations on the two limiting stereochemistries for five-coordinate cobalt(II) containing the same set of donor atoms, these two structures demonstrate that one must be very cautious in using electronic spectra to distinguish between square-pyramidal and trigonal-bipyramidal Co(II) complexes. Unless one were fortunate enough to isolate both the trigonal-bipyramidal and the square-pyramidal forms of a five-coordinate cobalt(II) system, it would be very difficult to evaluate definitively the relative intensity of the electronic absorptions in the $\sim$15,000-cm^{-1} region and to assign a structure to the five-coordinate complex. Optical spectra of single crystals of **1** and **2** will be examined to provide definitive assignments for the electronic transitions.

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Judith K. Stalick, P. W. R. Corfield, Devon W. Meek*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received May 25, 1972

Amide–Water Hydrogen Bonding

Sir:

Hydrogen bonding involving the amide linkage in proteins is clearly the most important feature of secondary (α-helical and β-sheet) structure.[1] Thus, it is of great interest to estimate the relative energies of peptide (C═O···H–N) hydrogen bonds and those involving water as a proton donor (O—H···O═C) or proton acceptor (N—H···O) to a peptide group. Several experimental studies[2,3] disagree somewhat on the comparative strength of amide H bonds and amide–H_2O H bonds so one would like to get an independent estimate of these H-bond strengths. Some progress in getting a theoretical estimate of the strength of the amide bond was made by Dreyfus and Pullman,[4] who computed the dimerization energy for a linear $H_2NCHO\cdots H$-NHCHO association of two formamides.

In this note, we report *ab initio* molecular orbital calculations (using an STO-3G basis[5]) on the linear formamide dimer $(H_2NCHO)_2$, two formamide–water dimers [$(H_2NCCH){=}O\cdots HOH$ and $CHONH_2\cdots OH_2$], formaldehyde–water ($H_2CO\cdots HOH$), ammonia–water ($NH_3\cdots OH_2$), and the water dimer. Using these results, we address ourselves to the following questions. (1) How competitive is a water molecule for an H-bonding site on a protein (N—H···O═C)? (2) How does the carbonyl of formamide compare with that of formaldehyde in base strength? (3) How much better a proton donor than NH_3 is the NH_2 group in formamide? (4) How do these STO-3G computed dimerization energies compare with those calculated with an STO basis [$(H_2O)_2$ and $H_2CO\cdots HOH$],[6] with an STO-4G basis $(H_2O)_2$,[7] with an LCAO-double ζ basis [$(H_2O)_2$[8] and $NH_3\cdots OH_2$[9]], and with a very extensive basis $(H_2O)_2$?[10] Answering this last question should give us an estimate of the reliability of the STGO-3 basis to predict dimerization energies.

The minimum energy geometries, computed dimerization energies, and Mulliken populations for the dimers are presented in Table I. It is clear that dimerization energies found using this STO-3G basis are essentially identical with those found using STO,[6] STO-4G,[7] and other[4] small contracted *ab initio* bases. A comparison with more exact calculations for water dimer[10] indicates that our calculated dimerization energies are probably $\sim$2 kcal/mol too high, although dispersion and zero point energy corrections[10] added to an exact SCF calculation might make our agreement with experiment slightly (0.5–1 kcal/mol) better.

We can, however, have confidence in *comparing* different H bonds; the differences in H-bond energy should be more accurate than their absolute value.

In considering our computed H-bond energies, we find that (1) the amide–amide N—H···O═C bond energy is considerably stronger than either amide–water bonds. The amide N–H group appears to be a 3.0 kcal/mol better proton donor than H_2O and the formamide C═O a 2.0 kcal/mol better proton acceptor than water in formamide H bonding. (2) In comparing formamide–water H bonding with formaldehyde–H_2O and ammonia–water, we find the formamide C═O to be a better proton acceptor than the aldehyde C═O by 3.05 kcal/mol and the amide to be a better proton donor than ammonia by 3.1 kcal/mol. (3) These results clearly show that one must apply the concept of "intrinsic" proton donor or acceptor strength with caution. If one extrapolated findings (1) and (2), one would predict that water is a better proton donor than ammonia by 0.1 kcal/mol and water is a better proton acceptor than formaldehyde by 1.05 kcal/mol. A direct comparison using the last three columns of Table I indicates that water is a 2.2 kcal/mol better proton donor than ammonia and a 3.3 kcal/mol better acceptor than formaldehyde.

The population analysis changes presented in Table I follow the trend previously noted for H-bonded systems.[11] In the general H bond A–X···H–Y–B, the A–X molecule transfers some charge to H–Y–B; the X actually gains electrons on H-bond formation (because it pulls more electrons away from A than it gives up) and the proton acceptor atoms (A) *all* lose charge.

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Table I. Dimer Results

		(Formamide)$_2$[a]		$H_2NC(H)=O$ HOH[b]		CHO–HNH OH_2[c]		H_2CO HOH[d]		H_2NH OH_2[e]		$(H_2O)_2$[f]
ΔE (dimerization), kcal/mol		9.4 (∼9)[4]		6.4		7.4		3.35 (3.45)[6]		4.3 (2.3)[9]		6.53 (6.65)[6] [4.8][10]
Minimum energy R, Å		2.80 (2.85)		2.75		2.7		(2.85)		2.8 (3.41)		(2.75) [3.0]
Minimum energy θ, deg		60 (∼60)		65		20		(64)		60 (0 assumed)		(54)
Proton donor populations[g]	N	7.4690 (−0.0226)	O	8.4678 (−0.0423)	N	7.4725 (−0.0261)	O	8.3889 (−0.0234)	N	7.5063 (−0.0364)	O	8.4085 (−0.0430)
	H_{Nc}	0.7928 (−0.0187)	H_b	0.8398 (−0.0225)	$H_{Nc(b)}$	0.7903 (−0.0162)	H_b	0.8285 (−0.0112)	H_b	0.8613 (−0.0179)	H_b	0.8389 (−0.0216)
	H_{Nt}	0.7580 (0.0310)	H	0.7889 (0.0284)	H_{Nt}	0.7546 (0.0344)	H	0.8009 (0.0164)	H	0.8103 (0.0331)	H	0.7911 (0.0262)
	C	5.7562 (−0.0049)			C	5.7554 (−0.0041)						
	H_c	0.9481 (−0.0039)			H_c	0.9540 (−0.0098)						
	O	8.3122 (−0.0171)			O	8.3111 (−0.0160)						
Proton acceptor populations[g]	N	7.7396 (0.0068)	N	7.4419 (0.0045)	O	8.3690 (−0.0035)	C	5.9072 (0.0110)	O	8.3618 (0.0037)	O	8.3653 (0.0002)
	H_{Nc}	0.7675 (0.0066)	H_{Nc}	0.7686 (0.0055)	H_1	0.7965 (0.0208)	O	8.2029 (−0.0102)	$H_{1,2}$	0.7995 (0.0178)	$H_{1,2}$	0.7981 (0.0192)
	H_{Nt}	0.7813 (0.0077)	H_{Nt}	0.7815 (0.0075)	H_2	0.7968 (0.0205)	H_1	0.9344 (0.0102)				
	C	5.7361 (0.0152)	C	5.7362 (0.0151)			H_2	0.9372 (0.0072)				
	H_c	0.9346 (0.0096)	H_c	0.9309 (0.0133)								
	O	8.3044 (−0.0093)	O	8.3075 (−0.0094)								

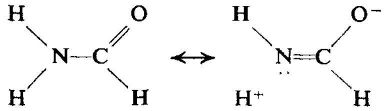
[a] The antiparallel geometry of Dreyfus and Pullman[4] was used. R is the O· · ·N distance; θ is the C=O· · ·N angle. The N–H· · ·O angle was assumed to be 180°. [b] R is the minimum energy O· · ·O distance; θ is the C=O· · ·O angle. The external hydrogen on the water was assumed trans to the C=O hydrogen; H_b refers to the hydrogen-bonded H. [c] R is the minimum energy N· · ·O distance; θ is the angle between the formamide plane and the HOH plane; H_{Nc} is the H-bonded hydrogen; H_1 is the water hydrogen cis to the other amide hydrogen. [d] R is the O· · ·O distance; θ is the C=O· · ·O angle; H_b is the H-bonded proton; H_1 is the hydrogen cis to the water; H_2 is trans to the water; the minimum energy geometry was assumed from ref 6 (values in parentheses). [e] R is the N· · ·O distance; θ is the angle between the HOH plane and the plane ⊥ to the plane bisecting the external HNH angle; values in parentheses from ref 9. [f] R is the O· · ·O distance; θ is the angle between the HOH plane and the O· · ·HOH plane (see ref 6 or 10 for complete geometry); we used the geometry of ref 6 for this calculation. [g] Differences in parentheses. – refers to increase in negative charge, gain of electrons; positive value means loss of electrons.

The H-bonded proton loses net charge on H-bond formation and Y and B both gain (B stands for *all* the rest of the atoms on the proton donor molecule).

Using the more complete variation in H-bond energy with O···N distance and C═O···N angle computed by Dreyfus and Pullman for linear formamide, we can conclude that a linear amide bond shorter than about 2.6 Å and longer than 3.4 Å is weaker than the completely optimized amide–water H bonds studied here. Thus, because of the geometrical constants imposed in carboxypeptidase,[1] some of its amide H bonds are weaker than optimum amide–water bonds.

These results should have considerable implications in the examination of secondary structure of proteins. In particular, model calculations of peptide conformation might now consider competitive amide–amide and amide–water H bonding in proteins; the H-bond energies found here should provide useful starting points for these potential functions.[12]

Also, by comparing the H-bonding ability of formamide, formaldehyde, and ammonia, we have provided the first semiquantitative estimate of the effect of the amide resonance structure



in increasing the H-bond base strength of a carbonyl group and the H-bond acid strength of an N–H bond.

Acknowledgments. One of us (P. A. K.) appreciates useful discussions with I. D. Kuntz.

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Allan Johansson
Department of Inorganic Chemistry
Helsinki University of Technology
Otaniemi 02150, Helsinki, Finland

Peter A. Kollman*
Department of Pharmaceutical Chemistry, School of Pharmacy
University of California, San Francisco
San Francisco, California 94122

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Germination Stimulants. II. The Structure of Strigol—A Potent Seed Germination Stimulant for Witchweed (*Striga lutea* Lour.)[1,2]

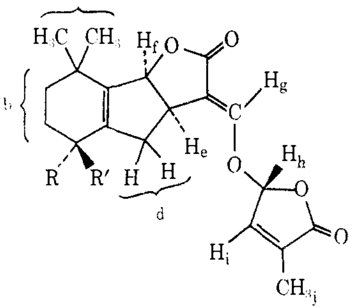
Sir:

We wish to report the structure of strigol (**1a**), a novel, highly potent seed germination stimulant isolated from the root exudates of cotton (*Gossypium hirsutum* L.).[2] In the absence of exogenous stimulant the seeds of the parasite witchweed (*Striga lutea* Lour.) do not germinate, but application of 10^{-11} *M* solutions of strigol results in over 50% germination.

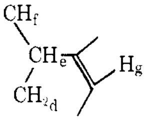
Witchweed is a chlorophyll-bearing parasite which attaches to the roots of corn and numerous other gramineous crops, causing severe damage. A native of the Eastern Hemisphere, witchweed was discovered in the United States in 1956 and is the object of a costly control program.[3] The demonstration that seeds of parasitic *Striga* species (and the related *Orobanche* parasites) require a chemical germination stimulant exuded from growing plant rootlets[4] led to numerous investigations of the nature of the stimulant or stimulants.[5] Until now, however, their structure has remained obscure.

Strigol [*m/e* 346.1408 ($C_{19}H_{22}O_6$ requires mass 346.1416), white needles from benzene–hexane, mp 200–202° dec] exhibited $\nu_{\max}^{CH_2Cl_2}$ indicative of OH (3590 cm^{-1}), butenolide (1787, 1745 cm^{-1}), and enol ether or unsaturated ketone (1682 cm^{-1}). Although a uv maximum at 234 nm (ϵ 17,700) was compatible with an unsaturated ketone, this moiety was ruled out by lack of a weak absorption band above 300 nm. The mass spectrum showed rapid cleavage to the fragments $C_5H_5O_2$[6] and $C_{14}H_{17}O_4$,[6] the latter undergoing facile dehydration to $C_{14}H_{15}O_3$.[6]

The nmr spectrum of strigol was highly characteristic, and in conjunction with spin decoupling experiments allowed the proton resonances to be unequivocally assigned. The geminal dimethyl groups (H_a) appear as singlets at δ 1.16 and 1.08,[7] the four cyclohexane methylene protons (H_b) at 1.52 (br), and the vinylic methyl (H_j) at 1.99 (t, J = 1.5 Hz). The cyclopentane methylene hydrogens (δ 2.67) (H_d, d) are essentially equivalent, but are coupled to H_e (J = 6 Hz). The latter resonance (δ 3.61) is also coupled to H_f (δ 5.48 (d, J = 8 Hz)), and allylically coupled to the highly deshielded proton H_g (δ 7.42 (d, J = 2.5 Hz)). Proton H_g may be compared with a somewhat analogous proton in plumericin.[8] Structural moiety **2** is thus firmly estab-



1a, R = H_c; R′ = OH
b, R,R′ = O
c, R = H; R′ = OAc



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