High-Level Electron Correlation Calculations on Formamide and the Resonance Model

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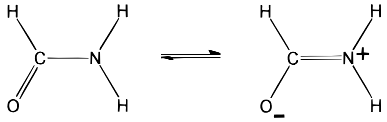
The question of planarity and the validity of the amide resonance model have been investigated in formamide on the basis of high-level quantum chemical calculations. Complete geometry optimizations were performed for the equilibrium structure and for the 90°-rotated transition state at the MBPT(2), MBPT(4), CCSD, and CCSD(T) electron correlation levels, with basis sets up to cc-PVTZ. While electron correlation tends to give nonplanar equilibrium, the final result at the CCSD(T)/PVTZ level is an *exactly* planar structure, as proven by the absence of imaginary vibrational frequencies. The crucial parameter in the geometry, the C−N bond length is calculated at 1.354 Å. For the barrier to internal rotation around the C−N bond our best estimate, including the zero-point-energy correction, is 15.2 ± 0.5 kcal/mol. To check predictions of the resonance model, we have analyzed geometric changes, charge shifts from Mulliken population analysis, and the nature of relevant valence orbitals and also calculated NMR chemical shieldings as a function of internal rotation. In contrast to recent suggestions by Wiberg *et al.* (*J. Am. Chem. Soc.* **1987**, *109*, 5935; **1992**, *114*, 831; *Science* **1991**, *252*, 1266) that π-resonance would not play a significant role in explaining the rotational barrier in formamide, we have found no compelling evidence to doubt the validity of the amide resonance model.

I. Introduction

The importance of formamide for structural chemistry and biochemistry is obvious: this is the simplest possible molecule containing the OCNH unit characteristic of the peptide bond. Two points are of primary interest about the structure of formamide: (a) the question of whether the equilibrium geometry is planar and (b) the magnitude of the barrier to internal rotation around the C−N bond. (The significance of planarity in reducing the number of conformational varieties in peptides is put in a nice historic perspective in a posthumous paper by Pauling.[1]) While the tendency of the amide moiety toward planarity—explained conventionally by the resonance model—is generally accepted, the possibility of a nonplanar peptide unit has been a recurring question since the classic studies by Ramachandran.[2,3] The existence of twisted amides in sterically constrained situations is well-known, and interpretation of their chemical and physical properties has strong relevance to the resonance model.[4,5] Most recently, the possibility of a pyramidal amide nitrogen in peptides has been brought up by Sulzbach *et al.*[6] in connection with calculated NMR shifts: the observed differences in chemical shifts between an α-helix and a β-pleated sheet could be reproduced only if the nitrogen environment was assumed to be nonplanar.

We emphasized already in an early paper[7] and it will be seen in detail below that *exact* planarity of formamide is an extremely delicate question. Experimentally, despite sophisticated microwave and infrared spectroscopic studies,[8−12] it seems virtually impossible to distinguish between a planar and a slightly nonplanar structure with a small hump on a flat potential surface. Theoretically, the results are sensitive to both basis set effects and electron correlation. Hartree−Fock calculations[7,13−16] may give both planar and nonplanar geometries, depending on the basis set in a rather random manner. Inclusion of electron correlation in the framework of second-order perturbation theory seems to lead to a preference of nonplanarity.[17−22] From density functional theory (DFT) both planar and nonplanar structures have been found, depending on the basis set and the choice of the exchange-correlation functional.[23,24]

The barrier to internal rotation around the C−N bond gives information about the nature of the amide bond and raised the interest of theoreticians long ago.[25,26] Experimental[27−30] and theoretical[21,22,24−26,31−38] values for the barrier vary in the range 15−20 kcal/mol, a fairly high value, clearly indicating the partial double bond. The well-known qualitative explanation of this double-bond character is based on the resonance model, as shown in the familiar scheme below:



When deciding that despite numerous previous studies a new theoretical study on formamide was worthwhile, we were led by two considerations. *First*, recent electron correlation calculations—although giving partly contradictory results—tend to suggest that higher levels of theory lead to nonplanarity. We find this somewhat counterintuitive. The *second* consideration may be even more important: in a series of influential papers Wiberg[35,37,39] has questioned the validity of amide resonance theory in explaining the barrier to internal rotation in formamide. This seems indeed very disturbing from the point of view of using qualitative models in structural chemistry. We have therefore decided to perform calculations on both the equilibrium structure and the 90°-rotated transition state, going as high as possible with the level of theory. Electron correlation in previous geometry optimizations was treated at the lowest level, second-order perturbation theory. We will present here results obtained from coupled cluster methods and fourth-order perturbation theory, using matchingly large basis sets (see details in the Computational Methods and Notation section). Beyond the figures obtained from these calculations, our main concern is a qualitative picture of the amide structure. We will analyze the results from various aspects: besides population analysis,

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nuclear magnetic resonance (NMR) chemical shieldings will be calculated to obtain information about charge shifts during rotation.

II. Computational Methods and Notations

All calculations were carried out by the ACES II program system.[40] Basis sets were systematically increased from double- and triple-ζ polarization (DZP,TZP)[41−43] through triple-ζ two-polarization (TZ2P)[44−46] up to the "correlation-consistent" polarized valence triple-ζ (cc-PVTZ)[47] basis set. The latter (referred to briefly as PVTZ in this paper) is a set specifically designed for electron correlation calculations and contains polarization functions including f-functions. For historic reasons, Cartesian (six-component) d-functions were used in the DZP, TZP, and TZ2P sets, while the PVTZ set contained spherical harmonic functions (five-component d's, seven-component f's). When referring to literature results, the usual notation of basis sets introduced by the Pople group will be used.[48] Electron correlation calculations were performed by many-body perturbation theory to second and fourth order and coupled cluster theory with singles−doubles and approximate triples: MBPT(2), MBPT(4), CCSD, and CCSD(T). (For the perturbation method we use here the notation favored in the ACES II program system; the alternative notation referring to Møller−Plesset partitioning (MP2, MP4) is equivalent and will be used as synonyms when discussing results from papers that used the latter.) Unless noted otherwise, all calculated data cited at a given level of theory refer to geometries *fully optimized at the same level*. Geometry optimization was based on analytic gradients available in ACES II for all levels mentioned above.[49−51] When calculating frequencies, second derivatives were obtained by numerical differentiation of the analytic gradient. This can be done in ACES II for each symmetry species separately, a great convenience when only the out-of-plane (a″) frequencies are needed to decide about planarity (see the Discussion section). Nuclear magnetic resonance (NMR) shieldings were calculated at the Hartree−Fock (HF) and MBPT(2) levels as available in ACES II,[52] on the basis of the gauge-invariant atomic orbitals (GIAO) method.[53,54] When studying internal rotation around the C−N bond, a system of coordinates termed "natural coordinates" were used, as obtained by the INTC program.[55,56] Constrained geometry optimizations along the internal rotation coordinate were carried out by Pulay's GDIIS method.[57,58] In the above tasks, an interface program[59] connecting the relevant programs from TX90[60] and ACES II[40] was used.

III. Discussion

A. Planarity and Equilibrium Structure. Planarity of formamide is an extremely delicate problem: while it is common knowledge that it is "essentially" planar, distinction between an exact planar and a slightly nonplanar structure seems very difficult. Experimental studies indicate this problem clearly: the classic microwave spectroscopic study by Kurland and Wilson[8] reported a planar structure; a few years later Costain and Dowling—using data on more isotopomers—concluded that the structure was slightly nonplanar;[9] later, Hirota *et al.*[10] used the microwave data of 11 isotopomers (including ^{13}C and ^{18}O data) to determine the structure. Concerning planarity, they fitted a quadratic−quartic potential along the NH_2 inversion angle to the low-frequency infrared data from King,[61] and this fitting gave no hump at the planar configuration, leading to the conclusion that the structure was "essentially planar". As an alternative approach, Hansen *et al.*[11] (this study includes acetamide and thioformamide, too) used a Fourier expansion in cosine functions along a torsional type coordinate to fit the low-frequency vibrations, with the conclusion that the equilibrium structure is "planar or very close to planar". The obvious difficulty with all these experimental studies is that several simplifications had to be made in the models: coupling with other modes as well as the kinetic effect (variation of the reduced mass) was necessarily neglected. A sophisticated attempt was made to remove these deficiencies, as far as possible, by Brown *et al.*[12] They reanalyzed all of the available spectroscopic data using a large amplitude motion (LAM) model in which the inversion coordinate is coupled with several other coordinates: the couplings with torsion and the C−N bond length were variable parameters, while some other couplings were estimated from ab initio calculations and fixed. Note that some primary geometry parameters were also fixed. The potential was of the quadratic−quartic type, but the results were so insensitive to the quadratic term that this was fixed at an estimated value. Their result is a very shallow single-minimum potential. While their analysis "accounts for all of the experimental data relating to planarity of formamide", we still feel that some uncertainty arises from the assumptions noted above.

The experimental difficulties just underline the significance of theoretical calculations on the structure. Early Hartree−Fock (HF) calculations including geometry optimizations go back to the 1970s.[7,13,14] In the light of present computational resources, these can hardly be considered as conclusive, but it is interesting to see how sensitive planarity is to the selection of the basis function set. The first systematic test was made by Carlsen *et al.*:[14] the smallest, STO-3G basis set gives non-planar structure, and the 4-31G basis predicts planarity, while a double-ζ basis with d-functions on the non-hydrogen atoms gives again a nonplanar geometry. (Note that the latter optimization fixed some geometry parameters.) Our early study[7]—in which planarity was already determined by calculating the out-of-plane force constant matrix, see below—gave exact planarity with the 4-21G basis set. Larger basis sets were tested later by Boggs and Niu.[15] Their largest basis set was valence triple-ζ type, augmented with two sets of d-functions on the heavy atoms and one set of p-functions on the hydrogens, and gave a nonplanar structure with dihedral angles up to 9−12°. The authors stressed the role of polarization functions in determining the structure. The importance of a balanced use of polarization functions is indicated by the calculations of Wright *et al.*:[17] with a DZ set augmented by heavy-atom d-functions only, they obtained dihedral angles up to 12°, while adding p-functions on the hydrogens led to planarity. Among the popular basis sets from the Pople group[48] of similar quality, both 6-31G* and 6-31G** give planarity.[18,36,37]

Before discussing the effect of electron correlation, a technical remark seems to be in order which is especially important when the structure is close to planarity, as will be seen in cases below. When testing planarity, the only reliable procedure is to optimize the geometry *within planar* constraint and then to check whether this stationary point is a minimum or a saddle point; the latter can be accomplished by calculating the vibrational frequencies, an imaginary value indicating a saddle point. Although the above should be well-known, one can find even in present day publications the wrong technique: start with a geometry without any symmetry and see if the optimization converges to a symmetric structure. The obvious problem is that this latter procedure—for numerical reasons—can never give an *exactly* symmetric structure.

The first electron correlation study that performed complete geometry optimization making use of the analytic gradient seems to be the one by Wright *et al.*[17] Their highest level calculation was of the MP2/DZP type and gave a structure with dihedral angles away from planarity by 2−3°. Because they did not

TABLE 1: Lowest Frequency Vibration (in cm^{-1}) of Planar Formamide[a]

basis set	SCF	MBPT(2)	MBPT(4)	CCSD	CCSD(T)
DZP	44.5	244.1i	292.1i	284.5i	300.7i
TZP	175.0	306.3i	357.6i	333.1i	362.5i
TZ2P	148.8	89.7i	193.1i	178.9i	203.8i
PVTZ	165.9	167.7	*b*	104.0	61.6

[a] Imaginary values indicate nonplanarity; for emphasis, these are underlined. [b] Not calculated.

use the technique described above, they needed extreme efforts to decide about planarity: they made a clever linear interpolation scan between a planar and non-planar structure, but this still leaves some uncertainty about the final accuracy. Tsuzuki and Tanabe[36] make the statement that all of the five levels of calculations they performed (HF with 6-31G, 6-31G*, and 6-31G**; MP2 with the latter two basis sets) give planar structures. This is true for the HF results, but is incorrect for MP2: for the MP2/6-31G** case, several papers quote explicitly an imaginary frequency,[18−21] at about 60i cm^{-1}. We didn't find the MP2/6-31G* value in the literature and calculated it to obtain $\nu = 117\text{i}$ cm^{-1}. An extreme example of the technical problem mentioned above is the result given by Kwiatkowski and Leszczynski:[20] using MP2 with the large basis set 6-311G(3df,-2p), they carried out optimization in a nonsymmetrical structure and report dihedral angles of 0.001° (!) for the equilibrium structure, with the conclusion that the "calculations predict such a small deviation from planarity of the molecule that it should be considered as a planar system". It seems obvious that this extremely small deviation from planarity can hardly be else than numerical error. To check this explicitly, we have optimized the structure in planar constraint and calculated the out-of-plane frequencies at exactly the same level of theory: the lowest a″ frequency is 187 cm^{-1} (with the other two at 655 and 1059 cm^{-1}). Thus, no imaginary frequency is found, proving that the structure is *exactly* planar at this theoretical level. Apart from this corrected result, the only planar structure at the MP2 level was reported by Burton *et al.*,[21] when they augmented the TZV2P basis set with f-functions on nitrogen (nitrogen only). The presence of f-functions in both studies should be noticed. The MP2/TZV2P structure in ref 21 and all other MP2 structures in the literature are nonplanar. Note specifically a result with a fairly large basis set: Olson *et al.*[22] obtained dihedral angles of 12−14° at the MP2(FC)/6-311++G** level. Their perturbation treatment used frozen core, which may also have some effect on the result; still, it is surprising that another recent study makes the opposite statement: Ventura *et al.*[62] mention in passing that their "own geometry optimizations agree with the available theoretical and experimental data in that formamide is planar". True that they are concerned mainly with tautomerism, rather than details of the geometry; still the remark about planarity is not justified in the light of the above discussion. Because they do not quote frequencies, we have checked this with their largest basis set: our own MP2/6-311++G(2d,2p) calculations give the following a″ frequencies: 69.9i, 635.9, 1053.2 cm^{-1} ($E = -169.608\,332\,9$ au), the imaginary value proving nonplanarity. We mention finally the only geometry optimization that went beyond the MP2 level. Ou *et al.*[38] (interested mainly in the rotational barrier) have optimized the ground state structure at the MP4/6-31G** level. They found dihedral angles of 5−7°, in line with the observation above that correlation prefers nonplanarity, but the basis set is obviously too small to give really conclusive results about higher correlation effects.

From the present study, the basic information about planarity is contained in Tables 1 and 2. Table 1 shows the lowest vibrational frequency for formamide (this is always the out-of-plane mode in which the amino twist and wagging coordinates are strongly mixed) at various levels of theory (see the Computational Methods and Notations section above). The results systematically show the effects of increasing basis sets and the inclusion of higher levels of electron correlation. While we mentioned above that smaller basis sets behave in a rather random way, the present results indicate that from a fairly high quality upward they all predict planarity at the Hartree−Fock SCF level. Electron correlation at the MBPT(2) level tends to prefer nonplanarity, as was already indicated by earlier studies in the literature. The new information is that the effect of electron correlation is indeed very systematic: higher levels of correlation strengthen the tendency toward nonplanarity, CCSD(T) giving the highest imaginary frequency in each case. Considering that these calculations represent fairly high levels of theory and are accordingly very expensive, one could easily stop at, say, the CCSD(T)/TZ2P level with the conclusion that high-level electron correlation calculations predict nonplanar structure for formamide. Then, however, we stressed our computational resources to extend the calculations to the PVTZ set (the highest level CCSD(T) calculation of the three out-of-plane frequencies with this basis, which includes f-functions on each heavy atom, takes 1−3 weeks on a powerful workstation, and needs about 4 Gbyte disk space). As seen in Table 1, the PVTZ basis leads back again to planarity even with highly correlated wave functions. (Note that the trend is still the same as with the smaller basis sets: larger correlation, which led there to *larger imaginary* frequencies, gives now *lower real* frequencies.)

When investigating planarity, it should be clear, however, that the question is somewhat academic. This is seen in the results listed in Table 2. The TZ2P basis set—at all levels of electron correlation—gives quite significant deviations from planarity in terms of the geometry parameters, as indicated by dihedral angles off from planarity by up to 10−12°. *Energetically*, however, these deviations are practically negligible: even the largest energy difference is only 50 cal/mol, less than 20 cm^{-1}. For comparison, an experimental estimate[9] for the hump was 370 cm^{-1}. In our results, even where nonplanar geometries were found, the zero-point energy of the lowest frequency out-of-plane vibration is definitely above the hump.

In conclusion, our results show that electron correlation tends to shift the structure toward nonplanarity, but the barriers at planarity are physically insignificant. More importantly, when correlation calculation is coupled with the use of correspondingly large basis sets (in which higher angular momentum functions seem to be a determining factor), the final result is an *exactly planar* structure for formamide.

We now discuss some aspects of the geometry, with the results listed in Table 3. Besides the highest level CCSD(T)/PVTZ results, lower level calculations are included to give an impression of convergence. From an inspection of basis set and electron correlation trends, a "best estimate" is also given; although the latter has obviously no strict foundation, it is intended to give a better overlook of the final results, and we think that within the conservative error limits this is indeed the best equilibrium geometry for formamide. For comparison with experiment we included the results of two microwave (MW) studies[9,10] and Kuchitsu's electron diffraction (ED) results.[63] Substitution structures (r_s) from MW studies are generally considered as good approximations of equilibrium structures. ED r_g structures are thermal averages but may be based on more complete information. There is no doubt that the results by Hirota *et al.*,[10] listed as r_s(2) in Table 3, represent the most complete microwave study, which included ^{13}C and ^{18}O data; still, in view of the fact that the Costain−Dowling study[9] already

TABLE 2: Testing Planarity Constraint in Formamide on Selected Parameters (TZ2P Basis Set)[a]

	MBPT(2)		MBPT(4)		CCSD		CCSD(T)	
parameter	C_s	C_1	C_s	C_1	C_s	C_1	C_s	C_1
geometry[b]								
CN	1.3589	1.3591	1.3635	1.3674	1.3581	1.3619	1.3621	1.3662
NH_c	1.0021	1.0024	1.0036	1.0048	1.0008	1.0019	1.0031	1.0042
NH_t	0.9997	1.0000	1.0015	1.0027	0.9984	0.9997	1.0008	1.0021
CNH_c	119.37	119.00	119.38	118.08	119.40	118.15	119.35	118.01
CNH_t	121.03	120.73	121.08	119.75	121.06	119.75	121.05	119.70
$OCNH_c$	(0)	5.4	(0)	10.4	(0)	10.2	(0)	10.5
$OCNH_t$	(180)	173.8	(180)	167.9	(180)	167.9	(180)	167.7
energy diff., (kcal/mol)[c]	0.002		0.041		0.031		0.049	

[a] C_s and C_1 indicate the point group symmetry; that is, C_s is the planar structure. [b] Two-, three-, and four-character symbols denote bond lengths (Å), angles (deg), and torsions (deg), the latter defined as the dihedral angle between the planes OCN and CNH; the subscripts c and t indicate cis(syn) and trans(anti) position of the hydrogen relative to the oxygen. [c] Energy difference between the planar form and the nonplanar minimum, all optimized.

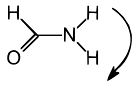
TABLE 3: Computed Equilibrium Structure of Formamide[a]

	MBPT(2)		MBPT(4)		CCSD		CCSD(T)		"best" theor.	exptl[b]		
Parameter	TZ2P	PVTZ	TZ2P	PVTZ	TZ2P	PVTZ	TZ2P	PVTZ	estimate[c]	$r_s(1)$	$r_s(2)$	r_g
CO	1.215	1.212	1.219	1.216	1.207	1.205	1.213	1.211	1.212(3)	1.193	1.219	1.212
CN	1.359	1.351	1.367	1.357	1.362	1.352	1.366	1.356	1.354(5)	1.376	1.352	1.368
CH	1.096	1.094	1.100	1.099	1.097	1.095	1.099	1.097	1.097(3)	1.102	1.098	1.125
NH_c	1.002	1.001	1.005	1.004	1.002	1.001	1.004	1.003	1.003(3)	1.014	1.002	1.027
NH_t	1.000	0.998	1.003	1.001	1.000	0.998	1.002	1.000	1.000(3)	1.002	1.002	1.027
OCN	124.7	124.9	124.7	125.0	124.7	125.0	124.7	125.0	125.0(2)	123.8	124.7	125.0
HCN	112.5	112.2	112.5	112.1	112.7	112.3	112.6	112.2	112.0(3)	113.2	112.7	(112.7)
CNH_c	119.0	119.2	118.1	119.3	118.2	119.3	118.0	119.3	119.3(3)	117.2	118.5	118.7
CNH_t	120.7	121.1	119.8	121.1	119.8	121.1	119.7	121.1	121.1(3)	120.6	119.9	(119.7)
HCNO	179.1	180	178.3	(180)	178.4	180	178.3	180	180	(180)	(180)	(180)
$OCNH_c$	5.4	0	10.4	(0)	10.2	0	10.5	0	0	7	(0)	(0)
$OCNH_t$	173.8	180	167.9	(180)	167.9	180	167.7	180	180	168	(180)	(180)
energy, $-(E + 169)$ (au)	0.614 134	0.648 816	0.655 326	0.690 991	0.626 964	0.659 645	0.650 753	0.685 855				

[a] For general notation and units see footnotes to Table 2; for the relative out-of-plane position of hydrogens note this: ABCD is the dihedral angle between the planes ABC and BCD, *irrespective* of bonding relations and using the following convention: the vectors perpendicular to the planes are defined as $n1 = e_{AB} \times e_{BC}$ and $n2 = e_{BC} \times e_{CD}$, the vector directions being $A \rightarrow B \rightarrow C \rightarrow D$. [b] $r_s(1)$ and $r_s(2)$ are substitution structures from microwave studies based on deuterium and ^{15}N data[9] and additional ^{13}C and ^{18}O data,[10] respectively; r_g structure from electron diffraction data combined with MW results.[63] Entries in parentheses indicate assumed, fixed values. [c] See text, with error estimates referring to the last digit.

was based on 10 isotopes (deuterium and ^{15}N substitutions), the large differences between the two results indicate the uncertainties of results often quoted simply as "experimental data". Among the individual parameters the CN bond length is of primary interest, as this is the crucial measure of the double-bond character. Our final estimate was established using the observation that increasing the basis set size and adding more correlation act in opposite directions. Note also that the longer CN bond in the TZ2P results is partly the consequence of the nonplanar geometry: as seen in Table 2, under planarity constraint the CN bond becomes shorter. (This coupling between the CN bond length and nonplanarity will be seen in more detail below in connection with internal rotation.) The final estimate around 1.354 Å agrees very well with Hirota's value of 1.352 Å.[10] We think that the other two results around or even above 1.37 Å are definitely too long. From the structural point of view, the CN bond length of 1.35−1.36 Å indicates clearly the partial double bond: for comparison, the corresponding experimental values in methanimine ($H_2C{=}NH$) and methylamine ($H_3C{-}NH_2$) are 1.273 and 1.471 Å, respectively.[64,65] As to theory, we have also optimized the geometries of these latter two molecules at the CCSD(T)/PVTZ level. The calculated CN bond lengths are 1.273 and 1.463 Å, respectively, in line with the above.

Another point of interest may be the angles around the nitrogen. In the theoretical results, comparison of the TZ2P and PVTZ values would indicate large uncertainty. This is misleading, however, as the lower angles in the TZ2P results are the direct consequence of pyramidality: accepting planarity, in the planar configuration TZ2P gives results practically identical with PVTZ; see Table 2. At the same time, correlation effects seem well converged concerning these angles. Thus, our final estimates seem reasonably justified. This means then a noticeable difference from Hirota's results: both of the CNH angles are larger in our results, and the consequence can be best expressed in the resulting HNH angle (being redundant, it is not listed in the table): the latter is 121.6° in the experimental study, while it is 119.6° in our study, staying close to the idealized 120°. On the other hand, there is good agreement in the following: both experiment and theory indicate that the NH_2 triangle is bent slightly (using the terminology of vibrational spectroscopy, along a rocking type coordinate) toward the oxygen, as sketched in the following scheme:



B. Internal Rotation and the Resonance Model. As is well-known from numerous theoretical studies, by rotating the amide group around the C−N bond by 90° and 270°, respectively, two transition states (TS) of C_s symmetry are obtained. These two are different due to the pyramidalization of the configuration around the nitrogen. We shall investigate here only the lower energy state (TS1), in which the hydrogens point toward the oxygen. This is the transition state determining the rotational barrier. TS1 is characterized by a low dipole moment of $\mu = 1.5{-}1.6$ D, as compared to $\mu \geq 4.0$ D for TS2.

TABLE 4: Computed Structure of the 90°-Rotated Transition State (TS1) of Formamide[a]

	MBPT(2)		MBPT(4)		CCSD		CCSD(T)		
parameter	TZ2P	PVTZ	TZ2P	PVTZ	TZ2P	PVTZ	TZ2P	PVTZ	Δ^b
CO	1.205	1.203	1.210	1.207	1.198	1.196	1.205	1.202	−0.009
CN	1.442	1.434	1.451	1.441	1.443	1.434	1.449	1.439	0.083
CH	1.093	1.092	1.096	1.094	1.093	1.091	1.095	1.093	−0.004
NH	1.014	1.014	1.016	1.017	1.013	1.013	1.016	1.016	0.014[c]
OCN	125.3	125.5	125.3	125.6	125.2	125.4	125.2	125.4	0.4
HCN	113.2	112.9	113.0	112.9	113.3	113.1	113.2	113.0	0.8
CNH	107.1	107.2	106.8	106.8	107.3	107.4	106.9	107.0	*e*
OCNH	55.7	55.7	55.3	55.4	55.9	56.0	55.5	55.6	*e*
rotational barrier,[d] ΔE (kcal/mol)	16.4	17.0	15.4	16.1	14.9	15.7	15.0	15.8	

[a] For general notation and units see footnotes to Table 2. [b] Geometry changes relative to the planar equilibrium, from the CCSD(T)/PVTZ results. [c] Average for the two hydrogens. [d] Energy difference from the corresponding minimum values in Table 3. [e] Angles around the nitrogen change, of course, drastically; it would be senseless to quote differences; see text.

TABLE 5: Typical Changes in Single and Double Bonds (Å) in Conjugated Systems[a]

	butadiene	iminopropene	glyoxal
$-\Delta S$ (C−C)	0.07−0.09	0.09−0.10	0.02−0.05
ΔD (C═X)	0.003−0.010	0.002−0.003[b]	0.001−0.003

[a] Based on a rough survey of experimental[71] and theoretical results.[72] For base molecules of "pure" single and double bonds ethane, ethylene, methanimine, and formaldehyde were considered. [b] Valid roughly both for C═C and C═N.

It was recognized from the beginning that for any reasonable calculation of the barrier it is inevitable to reoptimize the geometry for the transition state. This was very clearly shown by Nalewajski in early HF/4-31G calculations,[31] despite several limitations arising mainly from the lack of the gradient technique at that time (the planar structure was not optimized; the optimized parameters of TS1 seem also rather crude; notably the HNH angle of 132°—in the pyramidalized nitrogen moiety!—is obviously unrealistic.) The first Hartree−Fock ab initio studies performing reliable, complete geometry optimization of the transition state appeared around 1980[32,33] when the analytic gradient technique[66] became generally available. These studies (using the 4-31G and 4-21G basis sets, respectively) obtained 18−20 kcal/mol for the barrier, somewhat overestimated in the light of later results. They have still correctly established the basic structural changes upon rotation: pyramidalization of the amide group and lengthening of the CN bond. The role of electron correlation in *lowering* the barrier was shown very clearly by Jasien *et al*.,[34] although the transition state (TS1) was only SCF-optimized. Tsuzuki and Tanabe[36] have already optimized TS1 at the MP2/6-31G** level, and Wiberg and Breneman at the MP2/6-31G* level.[37] Burton *et al*.[21] used much larger basis sets and came to the conclusion that—if both the equilibrium and TS1 are optimized—the MP2 barrier is somewhat *larger* than the SCF one. Their result is 17.1 kcal/mol at the MP2/TZV2P+f (f-functions on nitrogen only) level. They too found lowering of the barrier down to 15.1 kcal/mol when using higher correlated (coupled cluster type) wave functions: in this case, however, the CCSD and CCSD(T) energies were calculated in the MP2 optimized structure, and the basis set was only 6-31G**. By adding a zero-point-energy (ZPE) correction (from MP2 calculations), their final best estimate is 61 kJ/mol (14.6 kcal/mol). Ou *et al*.[38,67] optimized the transition states with the 6-31G** basis set at the HF, MP2, and MP4 levels and obtained for the TS1 barrier, in this order, 16.0, 16.5, and 15.5 kcal/mol. An interesting fact in their results is that with MP4/6-31G** they found *two* imaginary frequencies in TS1, which would indicate a second-order saddle point. We think this must be an artifact, due to the small basis set. We have two sets of results available from our calculations related to this question: both the CCSD/TZP and the CCSD/TZ2P results show only one imaginary frequency, both at 492i cm^{-1}, and the next frequency is definitely real, at 887 and 891 cm^{-1}, respectively. Finally, Olson *et al*.[22] reported a barrier of 15.9 kcal/mol from MP2/6-311++G** calculations (TS1 also optimized), with ZPE correction (frequencies calculated at this same level) decreasing it to 15.2 kcal/mol.

Our results on the transition state are compiled in Table 4. Largely confirming previous lower level calculations, the structural changes upon rotation can be summarized as follows (when figures are quoted, they refer to the highest level, CCSD(T)/PVTZ results): (a) strong pyramidalization of the amide group; the OCNH torsional angle—which would be 90° for a rotated flat NH$_2$ group—is 55.6° (expressed in another way, the angle of the CN bond with the NH$_2$ plane is θ = 61.6°); of course, pyramidalization requires lowering of the angles around the nitrogen; besides the listed CNH angles of 107.0°, we add that the redundant HNH angle is 104.2°; (b) a very significant lengthening of the CN bond slightly above 0.08 Å; (c) a slight, but clear shortening of the CO bond by close to 0.01 Å; (d) finally, a lengthening of the NH bonds by 0.013 and 0.016 Å, respectively; this—often overlooked—change is certaintly quite significant for an X−H bond.

It is also of interest to compare the nitrogen moiety in the TS1 structure with methylamine. As mentioned above, we have optimized the latter at the CCSD(T)/PVTZ level. The relevant figures for methylamine are CN = 1.463 Å, NH = 1.011 Å, CNH = 109.4°, HNH = 105.8°, and θ = 56.5°. Comparing these with the results in Table 4 shows that the CN bond in rotated formamide is close to its counterpart in methylamine, but is still shorter by about 0.02 Å. Perhaps surprisingly, pyramidalization is even slightly larger in the transition state of formamide than in methylamine; *cf.* the two θ values above. As a general remark about pyramidalization, it may be noted that this strong coupling between torsion and inversion can already be seen close to the equilibrium planar structure. This was pointed out in our early vibrational study,[68] and we suggested that the lowest frequency vibration may be best described as a "twisting-pyramidal" mode.

For the rotational barrier our results vary between 15 and 17 kcal/mol. The strong basis set effect should be pointed out: even from the fairly large TZ2P basis, there is an *increase* of close to 1 kcal/mol when going to the PVTZ basis. As to correlation, the effect is again strong: when going from MBPT-(2) to higher levels, there is now a *decrease* of about 1 kcal/mol. The fact that the two effects act opposite explains that earlier lower level calculations gave very good (still perhaps slightly underestimated) results (14.5−15.5 kcal/mol).[36] For a comparison with experiment, zero-point-energy (ZPE) changes have to be considered. It would have been too expensive to do this at the highest level, but we have calculated the complete vibrational frequencies for the equilibrium and the transition state at two levels, *viz.*, MBPT(2)/TZ2P and CCSD/TZP. The

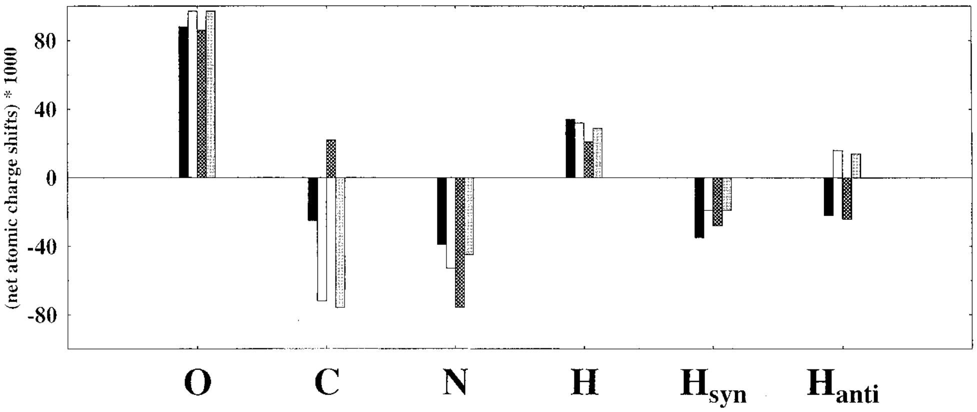


Figure 1. Atomic charge shifts (proton units) upon internal rotation in formamide from Mulliken population analysis. The bars indicate the difference between the 90°-rotated structure and the planar structure. Black, white, grid: MBPT(2) with basis sets DZP, TZ2P, and PVTZ, respectively. Gray: CCSD(T)/TZ2P.

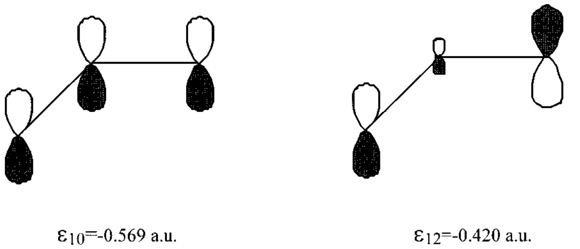


Figure 2. Schematic representation of the participation of p-atomic orbitals in the highest two a″ molecular orbitals in formamide (see text).

ZPE correction was found to be quite sensitive to the method, −0.4 and −0.7 kcal/mol, respectively. Considering these and taking the CCSD(T)/PVTZ barrier of 15.8 kcal/mol, our final estimate for the barrier with ZPE correction is 15.2 ± 0.5 kcal/mol. Experimental values for the barrier in various solvents vary in the range 17−22 kcal/mol.[27−29] As was discussed very clearly by Jasien *et al.*,[34] hydrogen bonds tend to increase the barrier so that theoretical calculations for the free molecule are expected to underestimate the barrier. Measurements by Chan *et al.*[30] in a polystyrene matrix may approximate the free molecule, but their result of 58 kJ/mol = 13.9 kcal/mol seems too low in the light of the theoretical results, of which the best seem to converge around 15.0−15.5 kcal/mol.

Our main interest in internal rotation in amides lies in the qualitative understanding of the amide bond. Traditionally, the partial double bond and the consequently high barrier are very simply explained by the resonance model. The well-known essential idea is that π-electron conjugation between the CO double bond and the nitrogen lone pair strengthens the C−N bond, leading to partial double-bond character, which is lost during rotation. The model thus relies on the π-electron system. As stressed in the Introduction, this simple picture has been seriously questioned by Wiberg *et al.*[35,37,39] They have two main arguments: (i) While the CN bond lengthening is indeed very significant upon rotation, the CO bond length changes very little; in addition, its value in the equilibrium shows no significant deviation from regular C=O double bonds. (ii) Calculating atomic electron populations based on Bader's method,[69,70] the charge shift on the nitogen atom is just the *opposite* of what the resonance model would predict, and the population at the oxygen is only slightly affected.

Their main conclusion is that "essentially all of the interactions leading to the rotational barrier originate in the C−N bond and that the oxygen does not participate to a significant extent."[37] The strengthening of the C−N bond is explained by hybridization arguments, related with the σ-system: "the C−N bond in the planar conformer has more ionic character, resulting in a shorter and stronger bond."[35]

About point i the following should be considered. It is a *general* observation in conjugated systems that the shortening of the single bond, ΔS, is about an order of magnitude larger than the lengthening of the double bond, ΔD. In Table 5 we have given a few examples based on a survey of experimental[71] and theoretical[72] results. Part of the large difference between ΔS and ΔD is understandable: if we compare the changes *energetically*, the larger force constant of the double bond involves a larger change in energy for the same change in the bond lengths. In the present example of formamide, we have checked this explicitly: in the rotated structure, with geometry optimized at the MBPT(2)/TZ2P level, a change of 0.01 Å in the C=O and C−N bonds back toward their values in the planar structure, the energy increase was $\Delta(E) = 144$ and 58 μhartrees, respectively. This brings down the ratio of about 9 in the bond length changes to a ratio of about 4 for the associated energy changes. This is, of course, still a large difference, and we do not see a simple model that could explain it. It may be added that the equilibrium C=O bond length in formamide *is* markedly, even if not drastically, longer than a "true" double bond. We checked this by calculating formaldehyde at the CCSD(T)/PVTZ level with the result of $R = 1.2065$ Å, which should be compared to the corresponding value of 1.2108 Å in formamide. Concerning the bond lengths, formamide thus behaves in every respect just like typical conjugated systems. Therefore, we think that point i does not really contradict the resonance model.

Point ii is of crucial importance concerning the use of qualitative models in structural chemistry. Obviously, when talking about partial charges and charge shifts in a molecule, one should always keep in mind that these are no physical quantities. There are still several well-known models trying to quantify chemically important notions, such as atomic charges and bond orders. Wiberg's conclusions[35,37] are based mainly on Bader's populations.[69,70] In our attempt to test charge shifts upon rotation from other aspects, we have first of all returned to the simplest, classic method of Mulliken.[73] It is, of course, well-known that electron populations can be very sensitive to basis sets (note that the results in ref 35 were based on one basis set only (6-31G**)). We have therefore evaluated the Mulliken populations from several of our calculations, with four typical results shown graphically in Figure 1. The bars indicate the shifts in atomic net charges when going from equilibrium to the TS1 structure (all structures optimized). As expected, the results show fairly large fluctuations, indicating the uncertainties of (any) population analysis. Still, in our opinion the overall picture is quite clear. (a) The most crucial problem in

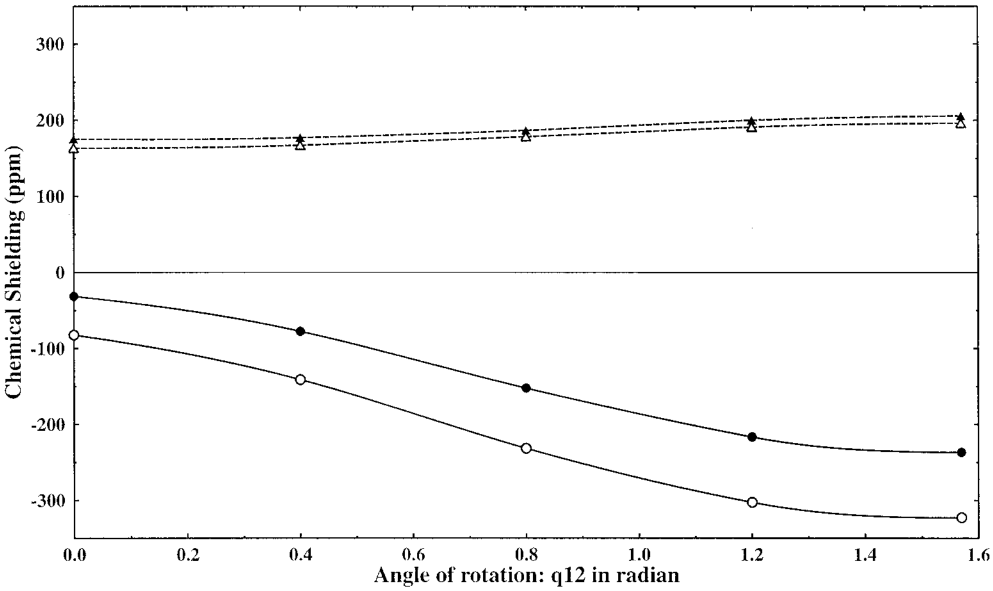


Figure 3. Calculated ^{17}O and ^{15}N NMR chemical shieldings as a function of internal rotation in formamide, with TZP basis on heavy atoms, DZP on hydrogens: circles, oxygen; triangles, nitrogen; white, SCF; black, MBPT(2).

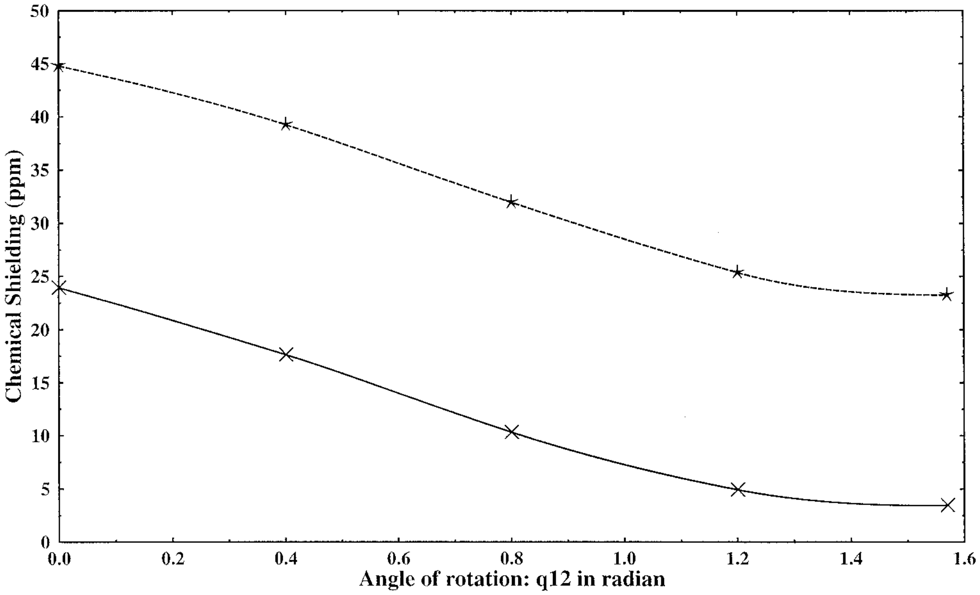


Figure 4. Calculated ^{13}C NMR chemical shieldings as a function of internal rotation in formamide, with TZP basis on heavy atoms, DZP on hydrogens: cross, SCF; star, MBPT(2).

Wiberg's results, in that they found negligible changes at the oxygen atom, is not present here; it is in fact the charge shift on the oxygen that is the most stable one in all four calculations. (b) Also, the nitrogen atom, although showing fluctuations up to a factor of 2, shows consistently negative charge shifts as predicted by the resonance model. (c) The charge shifts on the carbon atom fluctuate so much that no prediction can be given; still, this seems acceptable, as the resonance model does not say anything about it. Considering that the fundamental prediction of the resonance model concerns a positive charge shift from nitrogen to oxygen upon rotation and this is correctly reproduced, we hope to have proved that Mulliken population analysis—with all its limitations—does support the resonance model. It should be noted that population analysis based on the natural bond orbital concept of Weinhold[74] also clearly supports the resonance model, as shown by Ou *et al.*[38] In fact, this can even be seen in a most recent study by Wiberg,[75] concerned mainly with thioformamide.

It is also instructive to take a look at the relevant molecular orbitals. Taken at our MBPT(2)/TZP geometries, the highest three occupied SCF orbitals (10−12) and the first virtual orbital (with energies in atomic units given in parentheses) are as follows:

planar structure:
a″ (−0.569); a′ (−0.437); a″ (−0.420); a″ (+0.167)

rotated structure:
a″ (−0.524); a′ (−0.474); a′ (−0.441); a″ (+0.122)

In Figure 2 we show schematically the two occupied π-orbitals in the planar conformer. In orbital 10, the p-functions on the three heavy atoms participate with roughly equal weights; in orbital 12, the coefficients of the oxygen and nitrogen p's have opposite signs, and the carbon participation is very small. (The rotated structure is not shown, one of the a″ orbitals disappears, of course, and the remaining one is roughly the C=O bond.) The conclusion from Figure 2 about the planar structure seems very convincing about resonance: the character of these orbitals is the same as in the allyl anion, the archetypical example of a three-center-bond, resonance system!

The above discussion is based on qualitative–semiquantitative arguments. We thus tried to find true physical quantities that may give information about charge shifts during rotation. To this purpose we calculated NMR chemical shieldings as a function of internal rotation. The internal coordinates used in following internal rotation were the types suggested in ref 55. The rotational coordinate was then $q_{12} = (1/4)(\tau_1 + \tau_2 + \tau_3 + \tau_4)$, the sum of all four torsional angles around the C–N bond. (For the explicit definition of the rest of the coordinates, see ref 68.) For each point along q_{12} the rest of the geometry was optimized, at the level MBPT(2)/TZP. In the NMR calculations the basis set was TZP on heavy atoms and DZP on the hydrogens, and the calculations were done at two levels, SCF and MBPT(2). The results are shown in Figures 3 and 4. It is known that NMR shieldings are sensitive to correlation, and indeed the SCF and MBPT(2) results show very large differences. However, the *relative* values, i.e. the changes during rotation are practically the same. At the oxygen, the shift is very large and—using the simplified picture that decreasing shielding means decreasing electron density—is in the right direction. The shift at the nitrogen is much smaller, but again in the expected direction. The large shift at carbon is remarkable, but the resonance model says nothing about this. As a whole, since the amide resonance model concerns the nitrogen and oxygen, and the shifts on these latter are correct, the NMR calculations do support—at least do not contradict—the presence of resonance in formamide.

IV. Conclusions

We have presented theoretical results on formamide that, due to simply the advances in computational resources and the appearance of powerful computer programs, represent the highest level calculations on this molecule. On the basis of the results, conclusions can be drawn on qualitatively important aspects of the molecular structure.

(1) Systematically increasing the level of electron correlation, it has been shown that correlation strengthens the tendency toward a nonplanar equilibrium. This explains why the notion seems to have been spreading in the literature that the exact structure might be nonplanar (even if lying in an extremely shallow potential well). However, we find it very reassuring that using a matchingly large basis set, the highest level calculation (CCSD(T)/PVTZ) gives an *exactly* planar structure, in agreement with chemical intuition.

(2) In connection with calculating the barrier to internal rotation we have examined the well-known amide resonance model, which was seriously questioned in a series of articles by Wiberg.[35,37,39] We have discovered the following.

(a) Although the much smaller change in the CO bond length as compared to the CN bond cannot be explained in all detail, these two bond lengths behave the same way as in typical conjugated π-systems. Therefore, this behavior does not contradict the amide resonance model, unless the whole concept of π-resonance *in general* is denied.

(b) The charge shifts upon rotation from simple Mulliken population analysis, although showing fluctuations with the methods used, basically do support the resonance model. Especially important is the very consistent and uniform charge shift on the oxygen which, based on Bader's populations, was marked as a “spectator” atom by Wiberg.[75]

(c) Examination of the highest π-orbitals shows that formamide resembles very closely the electronic structure in allyl, a prototypical resonance system.

(d) NMR chemical shieldings, calculated as a function of internal rotation, are in line with the predictions of the resonance model for nitrogen and oxygen.

Keeping in mind the limitations of any qualitative model, we think that the present results do not give serious reason to doubt the validity of the amide resonance model as used traditionally in chemistry.

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