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Conformation Analysis of Formic Acid. Extended Basis Set SCF and CEPA Calculations

Constantin Zirz* and Reinhart Ahlrichs

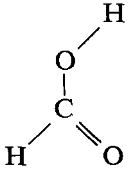
Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie und Elektrochemie, Universität Karlsruhe, Kaiserstr. 12, D-7500 Karlsruhe, Federal Republic of Germany

SCF computations using extended DZP and TZP basis sets have been performed to determine the structure of *syn* and *anti* formic acid and the transition state for rotation of the OH group. Effects of electron correlation were accounted for by means of CEPA calculations which predict the *anti* conformer to be 5 kcal/mol and the transition state 14.7 kcal/mol higher in energy than the *syn* conformer, with probable error estimates of 0.7 kcal/mol and 2 kcal/mol respectively.

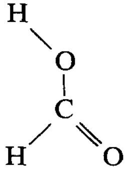
Key words: Formic Acid – Conformation analysis of ~.

1. Introduction

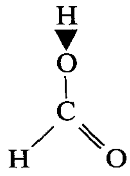
In the present paper we report extended basis set (DZP quality or larger) SCF and CEPA calculations for the *syn* and *anti* conformation of formic acid and the corresponding transition state arising in the OH rotation.



syn (= *trans*)



anti (= *cis*)



transition state (TS)

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* *Present address*: Firma BAYER AG, 5090 Leverkusen, Bayerwerk.

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The conformation analysis of gaseous formic acid has been the subject of numerous experimental investigations, which have recently been reviewed in Refs. [1–2]. However, when we became interested in this problem 3 years ago, reliable data were available only for the most stable *syn* conformer. The *anti* conformer has been definitely identified as late as 1976 [3], and estimates for the *syn-anti* energy difference ΔE_{Sa}

$$\Delta E_{sa} = E_{anti} - E_{syn} \tag{1}$$

and the barrier ΔE_B to the internal rotation of the OH-group

$$\Delta E_B = E_{TS} - E_{syn} \tag{2}$$

appeared to be still relatively uncertain. This situation has improved quite recently (actually during the time the present study was carried out), since the detection of formic acid in interstellar space [4, 5] has stimulated additional extensive microwave studies [2, 6]. The measurements of microwave spectra of various isotopically substituted species have led to an improved structure determination of the *syn* form [2] and the first such determination for the *trans* form together with more reliable results for ΔE_{sa} and ΔE_B [6].

Theoretical investigations of the above mentioned problems have been reported in various publications. The geometry of the (*syn*) ground state was determined on the SCF level by Del Bene et al. [7] in using an STO-3G basis and by Clementi and coworkers [8] with a DZ-type basis. Peterson and Csizmadia [9] have recently performed STO-3G calculations in order to determine the geometry of the anti conformer. These authors also published an STO-3G hypersurface giving the energy as a function of 3 structure parameters (O—H bond length, C—O—H angle and O=C—H dihedral angle) for which 3 other parameters (C=O and C—O bond length and O=C—O angle) were allowed to relax whereas the remaining 3 were frozen. Further studies of the OH-rotation in formic acid considered rigid rotation of the acid proton in assuming standard geometries or the structure parameters of the *syn* ground state [10–14]. These investigations have provided valuable insight into the changes of electronic structure during rotation – e.g. rearrangments in the π-electron system.

All theoretical treatments mentioned so far employed relatively small basis sets (no polarization functions) and were restricted to the SCF level. The only CI calculation for HCOOH was performed by Peyerimhoff and Buenker [15] at the equilibrium geometry to study the electronic spectrum.

In order to obtain more reliable theoretical results – especially for the *syn–anti* energy separation – we have performed extended basis set calculations (DZP and larger) on the SCF level and with inclusion of valence shell electron correlation.

2. Method of computation

The method of computation is best described as CEPA-2(SD), i.e. we have explicitly included all single and double replacements (from the valence shell) from the SCF reference function and have accounted for higher substitutions by means of the CEPA-2 approximation [16a–c]. From a more technical point of view our computational procedure is basically a matrix formulated direct CI [17] variant formally without complete integral transformation as described elsewhere [16c, 18] (only minor modifications of formulae and programs are necessary to go over from a CI(SD) to a CEPA(SD) variant). We have used CEPA-2 in this work since this variant (together with CEPA-1) seems to give the most reliable estimate of the contributions of higher than doubly substituted terms to the energy [16c, 18]. We point out that our theoretical method is closely related to Meyer's SCEP [19] and to the procedure developed by Pople and coworkers [20].

It may be worthwhile to give just one example of computation times involved in this sort of computations in order to give the reader an idea of computational expenses and of the efficiency of the programs used. In the treatment of the transition state of formic acid (no symmetry) with basis B – 55 CGTOs, see below – one has to deal with 75 465 singly and doubly substituted configuration state functions arising from excitations of the 9 valence MOs. Using double precision arithmetic and a scratch vector of 22 000 words this required ≈ 1.5 h computation time per direct CI-type iteration on a UNIVAC 1108. The CPU efficiency was 85% and the energy had converged to 10^{-4} a.u. in 5 iterations.

In this study we have mainly employed the following two basis sets of CGTO type

Basis A: (9 5 1, 5 1)/[5 3 1, 3 1]
Basis B: (8 4 1, 4 1)/[4 2 1, 2 1].

The primitive GTO bases were taken from Huzinaga's tables [21] and the orbital exponents η for polarization functions were chosen as $\eta_d(\mathrm{C}) = 0.75$, $\eta_d(\mathrm{O}) = 1.1$, $\eta_p(\mathrm{H}) = 0.65$. Basis B is of DZP and basis A of TZP quality.

3. Results and Discussion

We first determined the structure of the *syn* and *anti* conformers within the SCF method in using basis A which is of TZP quality. The molecule was assumed to be planar and the remaining seven parameters were obtained by means of a chain optimization. This iterative geometry optimization procedure was terminated after the energy was considered to have converged up to a possible error of a few tenth of a kcal/mol (in the given basis set and within the SCF approximation). This implies that bond distances may differ from converged ones by about 0.01 Å.

In Table 1 we have collected our results and compared them to recent, theoretical [7–9] and to the most recent and elaborate microwave results [2, 6]. With the exception of the C=O and C—O distances, the deviations between the present theoretical and the experimental structure parameters for the *syn* and *anti* conformer of HCOOH are in the order of errors of theoretical (as discussed e.g. in the preceding paragraph) and experimental methods (e.g. deviations between

Table 1. Experimental gas-phase and theoretical structures of formic acid conformers[a]

	C=O	C—O	C—H	O—H	O=C—H	O=C—O	O—C—H	C—O—H	
	1.201	1.340	1.091	0.969	123.3	124.8	111.9	106.6	exp[d]
syn[b]	1.178	1.319	1.086	0.951	124.3	124.9	110.8	109.4	This work
	1.214	1.378	1.102	0.991	125.5	124.2	110.3	105.4	STO-3G[e]
	1.215	1.332	1.085	0.970	—	—	—	114.0	Clementi et al.[f]
	1.195	1.352	1.105	0.956	123.2	122.1	114.6	109.7	exp[g]
anti[b]	1.172	1.328	1.093	0.946	123.7	122.4	113.9	112.2	This work
	1.211	1.382	1.108	0.988	123.4	121.4	115.2	106.4	STO-3G[h]
TS[c]	1.165	1.337	1.090	0.937	124.0	124.0	112.0	108.5	This work

[a] Distances in Å, angles in degrees.

[b] Planar (checked by additional calculations), see text for further details.

[c] Dihedral O=C—O—H angle 90° (assumed), CH proton −3° out of O=C—O plane, see also text.

[d] r_e values of microwave study, ref. 2. Error estimate is 0.005 Å for distances.

[e] Ref. [7] and [9].

[f] Ref. [8].

[g] r_s values of microwave study, Ref. [6].

[h] Ref. [9].

r_e and r_s values, see footnotes of Table 1 and Ref. [2]). We further note that the deviations are quite consistent, i.e. they are about the same for the *syn* and the *anti* conformer. This degree of agreement and consistency is not unexpected since SCF geometries obtained from DZP or larger basis sets are often very close to experiment. The C=O bond seems to be one of the exceptions to this rule. In a careful theoretical study of H_2CO Jacquet et al. [22] found complete agreement with experiment if electron correlation was included but the SCF result for the C=O distance was 0.03 Å too short. This is the same order of magnitude as the discrepancy found between the present SCF result and experiment (0.023 Å) for C=O in HCOOH, see Table 1. Our C—O distances are also about 0.022 Å smaller than the corresponding microwave results. Although it appears quite probable that this can be explained by the same reasoning as for the C=O distance, we cannot give a definite explanation for this fact at this moment.

The reliable determination of the transition state (TS) for the rotation of the OH group – defined as a saddle point of the hypersurface – would require the knowledge of the complete hypersurface in the vicinity of the TS geometry. Since such a procedure would have been too time consuming we simply fixed the O=C—OH dihedral angle at 90°, optimized the C—H and O—H distances, the C—O—H angle, and the out of plane bending of the CH proton with respect to the O—C=O plane. The remaining parameters were estimated in analogy to trends observed in auxiliary computations. It would only be fair to consider our TS structure as given in Table 1 as a good guess.

We finally performed CEPA-2(SD) calculations in order to determine the effect of electron correlation on the corresponding energy differences. To make these computations feasible we had to use Basis B for this purpose. From the numbers given in Table 2 we then get the theoretical energy differences on the corresponding level of approximation:

$$\text{SCF, basis A:} \quad \Delta E_{sa} = 5.4\ \text{kcal/mol} \tag{3}$$

$$\text{SCF, basis B:} \quad \Delta E_{sa} = 5.6\ \text{kcal/mol} \tag{4}$$

$$\text{CEPA-2(SD), basis B:} \quad \Delta E_{sa} = 5.2\ \text{kcal/mol} \tag{5}$$

Table 2. Computed energies for *syn*, *anti* and TS structure of formic acid [a]

Structure [b]	Basis set [c]	E_{SCF}	E_{CEPA}
syn	A	−188.82045	—
syn	B	−188.74718	−189.26926
anti	A	−188.81180	—
anti	B	−188.73824	−189.26105
TS	B	−188.72602	−189.24579

[a] Energies in au.

[b] See Table 1 for structure parameters.

[c] See text for detailed basis set description.

$$\text{SCF, basis B:} \quad \Delta E_B = 13.3 \text{ kcal/mol} \tag{6}$$

$$\text{CEPA-2(SD), basis B:} \quad \Delta E_B = 14.7 \text{ kcal/mol} \tag{7}$$

The SCF result for ΔE_{sa} obtained from the two basis sets differ by 0.2 kcal/mol only – Eqs. (3) and (4) – and even larger basis sets will probably change this number by at most a few tenth of a kcal/mol. Inclusion of valence shell correlation lowers ΔE_{sa} by 0.4 kcal/mol, compare Eqs. (4) and (5). This means mainly that electron correlation has a very small effect on ΔE_{sa} as could have been expected by virtue of the great similarity in electronic structure of the two conformers. If we combine Eq. (3) with the correlation effect obtained from Eqs. (4) and (5) we arrive at

$$\Delta E_{Sa} = 5 \text{ kcal/mol} \pm 0.7 \text{ kcal/mol} \tag{8}$$

where the probable error of 0.7 kcal/mol – an estimate based only on the authors' experience – should account for basis set and geometry optimization problems. Other theoretical values for ΔE_{sa} published in the literature [9–14] range from 4.5 kcal/mol [9] to 9.5 kcal/mol [11].

Our computed barrier ΔE_B for rotation of the OH group, Eqs. (6) and (7), is less reliable than the result for ΔE_{sa} since no rigorous geometry determination was performed for the transition state. Electron correlation appears to have a slightly more pronounced effect on ΔE_B than on ΔE_{sa}, but this effect is still relatively small. Our estimate for the probable error of ΔE_B is about 2 kcal/mol, yielding

$$\Delta E_B = 14.7 \text{ kcal/mol} \pm 2 \text{ kcal/mol} \tag{9}$$

Published theoretical values [9, 11–14] – exclusively obtained in using relatively small basis sets, e.g. without polarization functions – range from 9.6 kcal/mol [9] to 14.2 kcal/mol [11].

The present results for ΔE_{sa} and ΔE_B, Eqs. (8) and (9), support those of the most recent microwave investigation of Bjarnov and Hocking [6] ($\Delta E_{sa} = 4$ kcal/mol, $\Delta E_B = 13.8$ kcal/mol, without error estimates), and also older ones of Lide [23] ($\Delta E_{sa} > 4$ kcal/mol, inferred from the absence of an "*anti* microwave spectrum" under certain conditions) and Bernitt et al. [24] ($\Delta E_B = 13.4$ kcal/mol). They cannot be reconciled with previous experiments which seemed to indicate ΔE_B values of 17 kcal/mol [25] and 10.9 kcal/mol [26] and $\Delta E_{sa} = 2$ kcal/mol [26].

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References

1. Willemot, E., Dangoisse, D., Monnanteuil, N., Bellet, J.: J. Phys. Chem. Ref. Data, **9**, 59 (1980)
2. Wellington Davis, R., Robiette, A. G., Gerry, M. C. L., Bjarnov, E., Winnewisser, G.: J. Mol. Spectrosc., **81**, 93 (1980)

3. Hocking, W. H.: Z. Naturforsch., **31a**, 1113 (1976)
4. Zuckerman, B., Ball, J. A., Gottlieb, C. A.: Astrophys. J., **163**, 141 (1971)
5. Whiteoak, J. B., Gardner, F. F.: Proc. Astron. Soc. Aust., **2**, 360 (1975)
6. Bjarnov, E., Hocking, W.: Z. Naturforsch. **33a**, 610 (1978)
7. Del Bene, J. E., Worth, G. T., Marchese, F. T., Conrad, M. E.: Theor. Chim. Acta (Berl.), **36**, 195 (1975)
8. Bosi, P., Zerbi, G., Clementi, E.: J. Chem. Phys., **66**, 3376 (1977)
9. Peterson, M. R., Csizmadia, I. G.: J. Am. Chem. Soc., **101**, 1076 (1979)
10. Ros, P.: J. Chem. Phys., **49**, 4902 (1968)
11. Hopkinson, A. C., Yates, K., Csizmadia, I. G.: J. Chem. Phys. **52**, 1784 (1970)
12. Schwartz, M. E., Hayes, E. F., Rothenberg, S.: J. Chem. Phys. **52**, 2011 (1970)
13. Radom, L., Lathan, W. A., Hehre, W. J., Pople, J. A.: Aust. J. Chem., **25**, 1601 (1972)
14. Perricaudet, M., Pullman, A.: Int. J. Protein Res., **5**, 99 (1973)
15. Peyerimhoff, S., Buenker, R. J.: J. Chem. Phys., **50**, 1846 (1969)

16a. Meyer, W.: J. Chem. Phys., **58**, 1017 (1973). For recent reviews on CEPA and related methods see

16b. Kutzelnigg, W. in: Methods of electronic structure theory, ed. Schaefer, H. F. New York: Plenum Press (1977)

16c. Ahlrichs, R.: Comp. Phys. Commun., **17**, 31 (1979)

17. Roos, B. O., Siegbahn, P. E. M. in: Methods of electronic structure theory, ed. Schaefer, H. F. New York: Plenum Press (1977)
18. Zirz, C., Ahlrichs, R.: "Electron Correlation", Proceedings of the Daresbury Study Weekend, eds. Guest, M. F., Wilson, S. Science Research Council (1980)
19. Meyer, W.: J. Chem. Phys., **64**, 2901 (1976)
20. Pople, J. A., Binkley, J. S., Seeger, R.: Int. J. Quantum Chem., **S10**, 1 (1976)
21. Huzinaga, S.: "Approximate Atomic Functions I", Technical Report, University of Alberta (1971)
22. Jacquet, R., Kutzelnigg, W., Staemmler, V.: Theoret. Chim. Acta (Berl.), **54**, 205 (1980)
23. Lide, D. R.: J. Trans. Am. Crystallogr. Assoc., **2**, 106 (1966)
24. Bernitt, D. L., Hartman, K. O., Hisatsune, I. C.: J. Chem. Phys., **42**, 3553 (1965)
25. Lerner, R. G., Dailey, B. P., Friend, J. P.: J. Chem. Phys., **26**, 680 (1957)
26. Miyazawa, T., Pitzer, K. S.: J. Chem. Phys., **30**, 1076 (1959)

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