

Chemistry 433  
“Computational Chemistry”  
Winter Semester 1998  
Dr. Rainer Glaser

Second 1-Hour Examination  
“Extended Hückel Theory & Semi-Empirical MO Theory”

Wednesday, April 8, 1998, 8:00 - 8:50

Name:
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Question 1 (LCDs)	30	
Question 2 (CNDO vs NDDO)	20	
Question 3 (SE Parameters)	20	
Question 4 (HNO dimer)	30	
Total	100	

**Question 1.** Level Correlation Diagram and Extended Hückel Theory. (30 points)

In lecture, we discussed the paper “Non-Least-Motion Potential Surfaces. The Dimerization of Methylenes and Nitroso Compounds” by Roald Hoffmann et al., *J. Am. Chem. Soc.* **1970**, *92*, 1460, in some detail. For the nitroso compound, the dimerization can proceed in two ways in that the *cis* or the *trans* isomer can be formed (compounds **5** and **6** in the paper). The formation of **5** was discussed in the paper and a **level correlation diagram** was presented for this reaction in Figure 2 of that article. Here, we will be concerned with the level correlation diagram for the formation of the *trans* isomer via the least motion path.

(a) Draw Lewis structures of the *cis* HNO dimer. Make sure that you write down formal charges as appropriate. (Hoffmann *et al.* write the NO bonds as dative bonds. Give that Lewis structure. Then also give the Lewis structures in which the NO bonds are covalent.)

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(b) Symmetry Elements. Draw the *cis* and *trans* isomers of the dimer of HNO. For each isomer, indicate the **two** symmetry elements (mirror plane, rotational axis, inversion center) that are necessary to describe the **least motion paths** for the two dimerizations.

<i>Cis</i> Isomer	<i>Trans</i> Isomer

(c) For the construction of the level correlation diagram of the ***trans* isomer**, the six relevant orbitals are, on the **monomer** side, the two *N* lone pairs, and the  $\sigma$  and  $\pi^*$  levels of the two HNO groups. Sketch each of the associated orbitals (use p-AO and  $sp^2$  lobes, indicate phase information) and specify the symmetry of each orbital with regard to the two symmetry elements you chose in section (b).

-MO #1	-MO #2
n-MO #1	n-MO #2
-MO #1	-MO #2

(d) For the construction of the level correlation diagram of the *trans isomer*, the six relevant orbitals are, on the **product** side, the  $\sigma$  and  $\sigma^*$  MOs and the four  $\pi$  and  $\pi^*$  levels. Sketch each of these orbitals (use p-AO and  $sp^2$  lobes, indicate phase information) and specify the symmetry of each orbital with regard to the two symmetry elements you chose for the trans isomer in section (b).

-MO #1	-MO #2
-MO #1	-MO #2
-MO #3	-MO #4

(e) Construct of the **level correlation diagram** for the *trans* isomer. Give the HNO monomer levels on the left, give the HNO dimer levels on the right. Give the symmetry symbols for each level. Make sure that the ordering of the MOs is correct (high energy on top of page). Indicate occupancies of the orbitals with up & down arrows as usual. Connect the appropriate MO levels on the monomer and dimer sides.



**Question 2.** CNDO *versus* NDDO. (20 points)

(2 points) CNDO stands for:

(2 points) NDDO stands for:

(a) Briefly explain what “differential overlap” means. Your written explanation should be accompanied by an illustration. Pick a simple molecule, such as CO for example, for your illustration. (8 points)

(b) Briefly explain what part of “the hamiltonian” is most affected by approximate methods that neglect “differential overlap”. (8 points)

**Question 3. Semi-Empirical Parameters. (20 points)**

List five parameters which enter any of the semi-empirical theories you encountered in Chemistry 433 (EHMO, CNDO, CNDO/2, INDO, MNDO, AM1, PM3). Specify (1) the symbol and (2) the name of the parameter, (3) state how the parameter is determined (fitted to ..., derived from ...), and (4) state which part of the hamiltonian is determined by this parameter. (1 p. each part for each parameter)


**Question 4.** Computed Semi-Empirical Results on the HNO Dimerization. (30 points)

(a) The (rather long despite editing) supplementary material to this questions contains the output files of MNDO, AM1, PM3, and CNDO calculations of HNO monomer and of the *trans*-dimer. Go through these outputs and collect the data needed to complete the table. Then spend a some five minutes to compute the ***trans* preference energy** (state by how many kcal/mol the *trans* isomer is preferred; negative number if *cis* is more stable) and the **dimerization energy** (always compute for the *trans* isomer). (10 points for getting the table completed)

<b>Method</b>	E(HNO)	E( <i>Cis</i> -Dimer)	E( <i>Trans</i> -Dimer)	<i>Trans</i> -Preference Energy	Energy of Dimerization (for <i>trans</i> )
	in a.u.	in a.u.	in a.u.	in kcal/mol	in kcal/mol
<b>MNDO</b>	0.006011	0.100707	0.088688	7.54	48.11
<b>AM1</b>	0.003426	0.084729	0.066833	11.23	37.64
<b>PM3</b>	0.021961	0.088719	0.067787	13.68	14.98
<b>CNDO</b>	-30.741898	-61.655293	-61.662744	4.68	-112.29

(b) Discuss the data compiled in the table. State what you think are the best and the worst numbers and say why you think so. Be brief and concise and precise. (10 points)



(c) Now consider only the level you think is the best level among the four levels for this specific problem. Find the Mulliken populations of HNO and of the *trans* dimer. Comment on the electron density shifts that are associated with the formation of the dimer. (10 points)

For a recent discussion of the HNO dimerization, see: “Why Do Nitroso Compounds Dimerize While Their Oxime Tautomers Do Not? A Structural Study of the *trans*-Dimer of 2-Chloro-2-methyl-3-nitrosobutane and Higher Level ab Initio Study of Thermodynamic Stabilities and Electronic Structures of Configurational Isomers of Diazene Dioxides.” R. Glaser, R. K. Murmann, and C. L. Barnes *J. Org. Chem.* **1996**, *61*, 1047-1058.

*Na endlich ist der Test zu Ende!!*