250. The Interaction of Non-bonding Orbitals in Dicarbonyls: *Ab Initio* Results on Glyoxal

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Zusammenfassung. Die energetische Lage der kanonischen Molekelorbitale von Glyoxal in der *trans-* und *cis*-Konformation wurde durch *ab initio*-Rechnungen bestimmt. Die Wechselwirkung der «nichtbindenden» Orbitale dieser Molekel wird diskutiert.

Until recently spectroscopists have used simple $2p$-functions localized on the oxygen atoms to describe the non-bonding orbitals (n-orbitals) in dicarbonyl compounds [1]. Molecular orbital calculations [2] of the UV. and circular dichroism spectra by semi-empirical methods including all valency electrons indicate that such a description is, even qualitatively, insufficient. Experimental evidence from photoelectron spectroscopy [3], as well as from electrochroism measurements [4], supports this. However, semi-empirical calculations are in general subject to the arbitrariness

Table 1. *Orbital energies in* trans- *and* cis-*Glyoxal*[a])

	trans (C_{2h}) [b])	*cis* (C_{2v}) [b])
MO	– 20.6415 ($1a_g$)	– 20.6464 ($1a_1$)
	– 20.6415 ($1b_g$)	– 20.6464 ($1b_1$)
	– 11.5314 ($2a_g$)	– 11.5250 ($2a_1$)
	– 11.5308 ($2b_g$)	– 11.5244 ($2b_1$)
	– 1.4876 ($3a_g$)	– 1.4847 ($3a_1$)
	– 1.4620 ($3b_g$)	– 1.4542 ($3b_1$)
	– 1.0056 ($4a_g$)	– 1.0133 ($4a_1$)
	– 0.8689 ($4b_g$)	– 0.8385 ($4b_1$)
	– 0.7604 ($5a_g$)	– 0.7946 ($5a_1$)
	– 0.7113 ($5b_g$)	– 0.6826 ($6a_1$)
	– 0.6632 ($6a_g$)	– 0.6721 ($5b_1$)
π:	– 0.6317 ($1a_u$)	– 0.6269 ($1b_2$)
n:	– 0.5635 ($6b_g$)	– 0.5554 ($6b_1$)
π:	– 0.5458 ($1b_u$)	– 0.5404 ($1a_2$)
n:	– 0.4768 ($7a_g$)	– 0.4775 ($7a_1$)
E_T	– 226.24765	– 226.24288

[a]) Atomic units.

[b]) For the *cis*-form as yet unknown, we have chosen the standardized geometry: C–H: 1.08 Å, C–O: 1.22 Å, C–C: 1.5 Å, and $<$OCH: 120°.

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of the choice of empirical parameters. We have therefore effected an *ab initio* calculation[2] on glyoxal, the simplest α-dicarbonyl compound. Such a calculation should provide an unambiguous decision concerning the MO level ordering as well as the energy gap between the non-bonding orbitals.

Ab initio molecular wave-functions have been constructed with Gaussian lobe-functions as a basis set, with an accuracy equivalent to double zeta *Slater*-type orbitals

Table 2. n-*Orbitals in Glyoxal*[a])

	cis $[C_{2v}]$		*trans* $[C_{2h}]$	
	symm. $(7a_1)$	anti-symm. $(6b_1)$	symm. $(7a_g)$	anti-symm. $(6b_g)$
φ_{1s} (C1)	0.0157	–0.0334	0.0158	–0.0345
φ_{1s-2s} (C1)	0.0007	–0.0017	0.0007	–0.0018
φ_{2s} (C1)	–0.0433	0.2167	–0.0458	0.2217
φ_{2p_x} (C1)	0.3351	–0.0980	0.3324	–0.0908
φ_{2p_y} (C1)	–0.1191	–0.1585	–0.1242	–0.1551
φ_{2p_z} (C1)	0.0000	0.0000	0.0000	0.0000
φ_{1s} (C2)	0.0157	0.0334	0.0158	0.0345
φ_{1s-2s} (C2)	0.0007	0.0017	0.0007	0.0018
φ_{2s} (C2)	–0.0433	–0.2167	–0.0458	–0.2217
φ_{2p_x} (C2)	–0.3351	–0.0980	–0.3324	–0.0908
φ_{2p_y} (C2)	–0.1191	0.1585	0.1242	–0.1551
φ_{2p_z} (C2)	0.0000	0.0000	0.0000	0.0000
φ_{1s} (O1)	0.0014	–0.0091	0.0013	–0.0080
φ_{1s-2s} (O1)	0.0001	–0.0005	0.0001	–0.0004
φ_{2s} (O1)	–0.0080	0.0627	–0.0084	0.0593
φ_{2p_x} (O1)	–0.5790	–0.4941	–0.5871	–0.4896
φ_{2p_y} (O1)	0.2734	0.4505	0.2700	0.4508
φ_{2p_z} (O1)	0.0000	0.0000	0.0000	0.0000
φ_{1s} (O2)	0.0014	0.0091	0.0013	0.0080
φ_{1s-2s} (O2)	0.0001	0.0005	0.0001	0.0004
φ_{2s} (O2)	–0.0080	–0.0627	–0.0084	–0.0593
φ_{2p_x} (O2)	0.5790	–0.4941	0.5871	–0.4896
φ_{2p_y} (O2)	0.2734	–0.4505	–0.2700	0.4508
φ_{2p_z} (O2)	0.0000	0.0000	0.0000	0.0000
φ_{H1}	0.2156	0.1619	0.2121	0.1619
φ_{H2}	0.2156	–0.1619	0.2121	–0.1619
ε_i[b])	–0.4775	–0.5554	–0.4768	–0.5635

[a]) φ_{1s}, φ_{1s-2s}, φ_{2s} are the Gaussian group orbital basis set which represent the $1s$ and $2s$ *Hartree-Fock* atomic orbitals. For example the carbon $1s$ atomic orbital is composed almost entirely of φ_{1s} and the carbon $2s$ almost entirely of φ_{2s}, φ_{1s-2s} is intermediate. It is simply an additional basis function that makes possible a more perfect match of the atomic *Hartree-Fock* solution. The molecule lies in the xy-plane, C—C bond being the x-axis.

[b]) Atomic units, ε_i is the MO energy.

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[2]) Details on the wave functions and the *cis-trans*-isomerization process will be published elsewhere; *T.-K. Ha*, unpublished results.

[5]. The wave-functions employ 10 spherical *Gaussians* for the 1*s* and 2*s* orbitals and 5 pairs of Gaussians for each $2p_x$, $2p_y$, or $2p_z$ orbital of the carbon and oxygen atoms. Each hydrogen 1*s* orbital is represented by 5 spherical *Gaussians*.

Tab. 1 shows that the four highest occupied MO's are the two *n*- and the two *π*-orbitals, the sequence being *n*-*π*-*n*-*π*. We obtain for both *cis*- and *trans*-glyoxal an antisymmetric combination for the *n*-orbital below a symmetric one. The energy gap amounts to 2.36 eV in the *trans*- and 2.12 eV in the *cis*-form. The experimental value from photoelectron spectra is 1.6 eV [3].

The energy gap is nearly independent of the dihedral angle between the two carbonyl groups. A direct interaction between the 2*p*-orbitals on the oxygen atoms would place the symmetric combination below the antisymmetric one. The distance between the oxygen atoms being rather large in the *trans*-conformation (3.4 Å), we may consider the decrease of the energy gap by 0.24 eV in the *cis*-form to represent a rough measure of the "through space" interaction in *cis*-glyoxal. The value of 0.24 eV seems, however, rather large and considerably exceeds the values estimated from *Slater*-type orbitals [1].

The eigenvectors of the two *n*-orbitals are shown in Tab. 2. The values given provide means for a qualitative understanding of the large energy gap between the two *n*-orbitals: Contour diagrams[2]) of the electronic charge distribution for these orbitals show that, in contrast to the higher lying orbital, the lower one is devoid of nodes bisecting the C-O bonds.

Based on experimental findings we thus show definitely that the mechanism of the interactions of non-bonding orbitals in dicarbonyl compounds is "through bond" rather than "through space".

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