Theoret. Chim. Acta (Berl.) 40, 81–83 (1975)

Cis-trans Isomerization of Glyoxal

A Contribution to the Rehabilitation of Semiempirical Methods

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Received December 27, 1974/June 27, 1975

The CNDO/2 method with the original parameter set predicts the conformation with the mutually perpendicular CH=O groups to be the most stable isomer of glyoxal; the cis form is favoured over the trans form. The order of stabilities is not changed upon the full optimization of coordinates of the isomers. Calculations fail to reproduce the observed order of isomer stabilities unless allowance is made for limited configuration interaction with the lowest $\pi\pi^*$ doubly excited state and for geometry optimization. Doubly excited configurations of the $n\pi^*$ and $\sigma\sigma^*$ types have negligible effect on the energies of isomers.

Key word: Glyoxal, cis-trans isomerization of ~

Soon after the semiempirical methods have been developed, reports on their failures in some conformational problems appeared in the literature. The cis-trans isomerization of glyoxal [1] was among the first cases reported. Experimentally [2, 3], the most stable form of glyoxal is the trans conformation. The second rotamer identified [3], presumably a planar cis form, is 3.2 ± 0.3 kcal/mol higher in energy than the trans form. Unlike the *ab initio* calculations [4], CNDO/2 fails to give a correct order of energies of rotamers. For experimental bond lengths and bond angles [2] it predicts [1] the most stable form to have a torsional angle of about 90°, in disagreement with experiment. This can be seen in Table 1. The second line in Table 1 refers to the case where all geometry parameters of the cis, trans and twisted rotamers were so optimized as the energy gradient be vanishing [5, 6]. The energy difference between the trans and twisted rotameters decreased from 0.08 to 0.05 eV but the twisted form is still predicted to be the most stable conformation. The geometry optimization brings about energy lowering of 1 eV. Remarkably enough, this is 20 × higher than the height of the computed barrier.

In this paper an attempt was made to improve the results by taking into account a simple configuration interaction. For this purpose calculations were performed on the interaction energies between the ground state and the doubly excited states which may be derived formally by two-electron promotions from a bonding MO to an antibonding MO. With planar rotamers only the $\pi\pi^*$ configurations were found to be of importance. The ground state lowering brought about by them

Table 1. Energies of stationary points for the cis-trans isomerization of glyoxal. All values are in eV

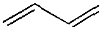
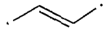
geometry optimization	LCI	cis	perpendicular	trans
–	–	–1421.431	–1421.508	–1421.427
+	–	–1422.576	–1422.606	–1422.554
+	+	–1423.166	–1422.634	–1423.195

was one order higher in energy than the energy decrease which was due to $n\pi^*$, $\sigma\pi^*$, $\pi\sigma^*$ and $\sigma\sigma^*$ configurations. With a twisted rotamer the effect of all doubly excited states was negligible. The third line in Table 1 represents the calculation of the rotational barrier in which allowance was made for configuration interaction with the lowest doubly excited $\pi\pi^*$ state and all molecular coordinates were optimized. Now, the order of rotamer stabilities is in agreement with experiment, though the E_{cis}–E_{trans} difference of 0.7 kcal/mol is considerably lower compared to the experimental value. Our results suggest that the effect of doubly excited configurations of this type will be negligible with σ-electronic systems. Since the CNDO/2 empirical parameters have been adjusted just with σ-electronic systems, it may be assumed that the inclusion of doubly excited states is not contradictory to the original semiempirical nature of the method. The optimized geometries of rotamers are given in Table 2. For the internal rotation of polyenes two cases should be distinguished. Recently it was shown with the cis-trans isomerization of ethylene [7] that no meaningful description of the twisted rotamer is possible unless inclusion of doubly excited states is accounted for. A different nature of our problem becomes evident even by using the reasoning based on the simple Hückel method. On twisting a polyene round a formal double bond one arrives at two odd alternant subsystems [8], where two electrons are available for two nonbonding MOs. This is the case of biradical with a vanishing $E(N\rightarrow V_1)$ gap. Upon the rotation round a formally single bond HOMO and LFMO are not degenerate any longer. In our case HOMO is degenerate but occupied by four electrons. As the $E(N\rightarrow V_1)$ gap is large, the interaction between frontier orbitals is insignificant and the one-electron approach to the twisted rotamer is justifiable.

Table 2. Optimized geometries of the stationary points on the section of the energy hyper-surface for the cis-trans isomerization of glyoxal. CNDO/2 was used with and without the inclusion of the limited configuration interaction with the lowest π-π^* doubly excited configuration[a]

	cis		twisted		trans		exp.[b]
	without CI	with CI	without CI	with CI	without CI	with CI	
r(C–H)	1.119	1.120	1.122	1.123	1.120	1.119	1.116
r(C–C)	1.435	1.429	1.433	1.433	1.437	1.430	1.525
r(C–O)	1.262	1.270	1.259	1.259	1.261	1.271	1.207
∢ HCC	119.6	118.2	114.7	114.8	119.1	119.9	112.2
∢ OCC	123.1	125.4	127.3	127.3	123.6	122.8	121.2
∢ OCCO	0.0	0.0	90.8	95.8	180.0	180.0	180.0

[a] Bond lengths in Å, angles in degrees.
[b] Ref. [2].

The interaction with the lowest $\pi\pi^*$ configuration may be taken as the interaction of the ground state structure  with the structure  , which brings about a stronger bonding on the formal single bond. This affords an explanation as to why the inclusion of LCI leads to the stabilization of planar rotamers.

Acknowledgement. The author wishes to thank Dr. R. Zahradník for his helpful comments and keen interest in the work.

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