



On the potential energy surfaces of dimers formed between *trans*-glyoxal, *trans*-acrolein and formaldehyde



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ABSTRACT

The potential energy surfaces of the six dimers formed between *trans*-glyoxal, *trans*-acrolein, and formaldehyde were investigated theoretically at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels. All in all thirty-five low-lying stationary points were detected. In five cases the global minimum of each dimer type has a non-planar structure. The acrolein dimer is the only case in which a planar arrangement prevails. Most dimers display geometry changes and vibrational frequency shifts characteristic for a formyl group engaged in hydrogen bonding or in more general intermolecular interactions: red shifts of C=O stretches and blue shifts of C–H stretches. The size of these shifts depends, however, strongly on the individual case.

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1. Introduction

Glyoxal (ethanedial), the simplest dialdehyde, acrolein (propenal) and formaldehyde (methanal) play all an important role in atmospheric chemistry as reaction products of various oxidation processes [1,2], for a variety of photochemical reactions [3,4], and as building blocks for the formation of secondary organic aerosols and organic particulate matter [5–10]. In general, aldehydes have also a strong tendency to polymerize and to form hydrates [11,12]. Both, glyoxal and acrolein, have two stable conformers, *trans* and *cis*. The *trans*-glyoxal conformer is about 20 kJ mol^{−1} more stable [13]. In the case of acrolein, the *trans*–*cis* energy difference is smaller and amounts to about 8.6 kJ mol^{−1} [14]. Only a few theoretical studies on hydrogen bonding or on alternative intermolecular interactions involving *trans*-glyoxal (Gly) or *trans*-acrolein (Acr) are available. Intermolecular complexes of Gly or of Acr with H₂O [15–20], with HF and BrF [16], and with the O₂H radical [21] as interaction partners have been investigated earlier applying either ab initio or density functional (DFT) methods. The only previous theoretical investigation on the (Gly)₂ dimer is due to Solimannejad et al. [22]. Quite recently, a systematic theoretical study of several aldehyde homodimers containing also results for the (Acr)₂ dimer has been published by Thakur et al. [23]. Experimental studies on the gas phase structures of (Gly)₂ or (Acr)₂ or matrix-spectroscopic data of these dimers are not yet available.

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The previous calculations on intermolecular complexes involving Gly or Acr, have shown that, despite the absence of a strong hydrogen bond donor, the interaction energies are in the range or even larger than in water dimer. Most of the interactions are dominated by the C=O bond that acts as a strong acceptor for hydrogen bonding or, e.g., also for halogen bonding [16]. The same is to be expected for the interaction between two Gly and two Acr molecules. Conceivable and energetically favorable structures could, therefore, either involve C–H···O=C hydrogen bonding, or, additionally, contributions from π -type hydrogen bonding to the C=O group. Even structures with π – π interactions could play a role. The calculations on Gly–H₂O complexes [16,17,20] provided evidence that non-planar, partially π -type complexes are energetically competitive to planar structures dominated by hydrogen bonding to the C=O group. As is well known, already the lowest-energy dimer of the simplest aldehyde, formaldehyde (FA)₂, has a structure in which the two monomers are oriented in planes perpendicular to each other [24–31]. Similarly, stable, non-planar configurations have also been calculated for dimers of other simple aldehydes [23,30,33–36].

C–H···O hydrogen bonding is often connected with blue shifts of the C–H stretching frequencies. Both phenomena have been studied quite intensely for more than a decade [37–52]. These blue shifts may arise when the C–H bond, or more generally, the X–H bond is directly involved in a hydrogen bond (blue-shifting). However, a blue shift may occur also when a remote hydrogen bond or some other intermolecular mechanism, e.g. a halogen bond, is present that involves a bond vicinal to the X–H bond

(blue-shifted). In cyclic complexes both types may be found simultaneously. In the case of aldehydes this vicinal bond is the C=O bond.

Undoubtedly, red-shifting as well as blue-shifting or blue-shifted hydrogen bonds can be rationalized by the conventional theory of intermolecular interaction. Quite similar electron density rearrangements are calculated [38–43]. In most cases, blue-shifting hydrogen bonds are encountered in cases of weak intermolecular interactions. Therefore, the most promising and at the same time also *predictive* explanations for the occurrence of blue vs. red shifts are based on an analysis of intramolecular properties of the molecule that displays the frequency shifts in the complex, rather than on *a posteriori* wave function analyses of the already formed complexes. The origin of the blue shift must have intramolecular roots. Attempts in this direction have been to inspect (i) the molecular, in particular, the structural response to external electric fields [37,40,45,46], (ii) the sign of the dipole moment derivative, $\partial\mu/\partial r(X-H)$ [39,45], and (iii), more directly connected to the potential energy surface (PES), the coupling between vicinal X–H and X–A bonds as calculated either with the aid of selected scans of X–H and X–A bonds [16,53–59], or equivalently by conventional normal coordinate analysis [16,60–62].

In this work, the intermolecular PESs of the homodimers (Gly)₂ and (Acr)₂ are investigated with the aim to search for the most stable minima, to clarify whether non-planar structures can compete energetically with planar arrangements, and to analyze the vibrational spectroscopic consequences for the C–H and C=O stretching frequencies of the formyl groups. In order to arrive at a more complete picture, analogous calculations are also performed for the well-known dimer of formaldehyde (FA)₂, and for the three mixed dimers or heterodimers Gly–Acr, Gly–FA, and Acr–FA. To the best knowledge of the author, experimental gas phase structure determinations are not available as yet for these aldehyde dimers, except for the well-studied case of (FA)₂. The current investigation is also the first theoretical study of the three heterodimers Gly–Acr, Gly–FA, and Acr–FA.

2. Computational methodology

All structure optimizations on the complexes were performed within the second-order perturbation Møller–Plesset frozen-core method (MP2) [63] in conjunction with the aug-cc-pVTZ basis set using the GAUSSIAN 09 suite of programs [64]. Due to the floppy nature of the studied complexes, all geometry optimizations were executed with the TIGHT option. Additionally, single point CCSD(T) [65–69] calculations were carried out for the optimized structures. Optimizations were conducted with and without explicit counterpoise (CP) corrections to the basis set superposition error (BSSE). This computational level is certainly sufficient for our purposes and should yield reliable results for structures and energies, which could be the basis for future, more accurate studies on individual dimeric aldehyde complexes.

In addition, Natural Bond Orbital (NBO) analysis [70] was performed using the SCF density.

3. Results and discussion

3.1. Structures and stabilization energies of the stationary points of the homodimers (Gly)₂, (Acr)₂, and (FA)₂

3.1.1. The monomers

For the understanding of the intermolecular interaction between molecules it is important to inspect the leading electrostatic properties of the molecules in question. The MP2/aug-cc-pVTZ calculated dipole moments of Gly, Acr and FA are 0 by symmetry, 3.25, and

2.40 D, respectively. Averaged dipole polarizabilities increase in the series FA, Gly, Acr as 18, 31, and 42 bohr³. The MP2/aug-cc-pVTZ calculated bond distances of Gly, Acr, and FA monomers have already been documented earlier [8,55]. Optimized C=O/C–H bond distances are 1.2146/1.1012 Å for Gly, 1.2189/1.1063 Å for Acr, and 1.2129/1.1002 Å for FA, respectively. As with all aldehydes, the C–H distance of the formyl group is distinctly longer than C–H distances in alkanes or alkenes, a feature ascribed to the non-acidic or even slightly hydridic nature of the formyl H atom [23]. The comparatively long C–C distance of 1.5149 Å indicates that Gly does not have a strongly delocalized π -system. Acr has with 1.4694 Å a much shorter C–C bond length, comparable to butadiene (1.4528 Å).

For the interpretation of the structural changes taking place upon complex formation, the coupling between C–H and C=O bonds within the formyl group is of central importance. This is shown in Fig. 1 for the Gly molecule. Lengthening of $r(C=O)$, e.g. induced by intermolecular association, leads to a shortening of $r(C-H)$ and vice versa. The behavior that the numerical derivatives $\Delta r(C=O)/\Delta r(C-H)$ and $\Delta r(C-H)/\Delta r(C=O)$ are negative has been termed *negative intramolecular coupling* (NIC) [16]. On the other hand, NIC usually corresponds to a positive off-diagonal harmonic force constant, $k_{C-H,C=O}$, which equals to 0.45 mdyn Å⁻¹ for Gly and 0.53 mdyn Å⁻¹ for Acr at the MP2/aug-cc-pVTZ level [16]. The very same behavior has already been reported earlier for the formyl group of FA [55,59]. The MP2/aug-cc-pVTZ calculated value for $k_{C-H,C=O}$ is 0.51 mdyn Å⁻¹. Early Hartree–Fock derived, scaled quantum mechanical force fields led to very similar coupling constants (0.33, 0.42, and 0.42 for Gly, Acr, and FA, respectively [71]).

3.1.2. The glyoxal dimer (Gly)₂

The MP2/aug-cc-pVTZ calculated structures of the stationary points of (Gly)₂, (I–VIII), of (Acr)₂, (IX–XVI), and of (FA)₂, (XVII),

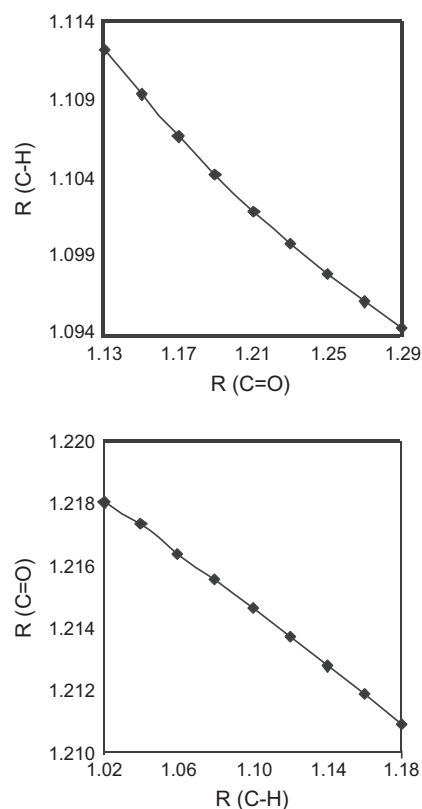


Fig. 1. MP2/aug-cc-pVTZ optimized C–H (C=O) distances obtained upon scanning the C=O (C–H) distance. All distances are given in Å.

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