

ROTATIONAL BARRIERS AND STABLE ROTAMERS IN 1,3-BUTADIENE, ACROLEIN AND GLYOXAL[†]

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ABSTRACT

Analytic gradient (Force) methods (ref.1) have been used to optimize completely the geometries of the title compounds at the minima (stable rotamers) and maxima (transition states, TS) in the torsional potential energy curves (TPEC) for rotation about the single C - C bonds. Computations were performed with the minimal STO-3G, split-valence 3-21G and polarized 6-31G \times basis sets for 1,3-butadiene and glyoxal, and with only the STO-3G and 3-21G basis sets for acrolein. Whereas complete geometry optimization of 1,3-butadiene along the TPEC with the STO-3G basis led to the prediction of a cis - trans rotamer equilibrium (ref.2), complete optimizations with both the 3-21G and 6-31G \times basis sets give a maximum at the cis position and minima at the trans and gauche conformations. Complete geometry optimization of acrolein reveals only cis and trans minima with the TS at 88.2(STO-3G) or 91.6(3-21G) degrees from the cis. Surprisingly the cis and trans conformers are predicted to be almost equivalent in energy. For glyoxal the TS is revealed to be nearer to the cis than to the trans conformation. Except for 1,3-butadiene, the barrier height to rotation from the trans position, obtained with the STO-3G basis, is much smaller than that obtained with the larger basis sets.

INTRODUCTION

The relative energies of stable rotamers of conjugated molecules and the barriers to rotation about the single C - C bonds in them are of considerable interest. In a previous paper (ref.2), the importance of complete geometry optimization on the form of the TPEC was emphasized. The choice of basis set has been shown to be important in studies on vinylcyclopropane (ref.3) and on cyclopropanecarboxaldehyde (ref.4). The present paper extends the data on 1,3-butadiene to larger basis sets and includes the isoelectronic species acrolein and glyoxal.

[†]In this paper the s-cis and s-trans conformers will be referred to simply as cis and trans, respectively.

METHOD

All calculations were performed using the MONSTERGAUSS ab initio program (ref.5) on the CYBER 170/750 computer system at the Université Libre de Bruxelles. Details on the methods used and references for the basis sets may be found in refs. 2-4.

RESULTS AND DISCUSSION

1,3-Butadiene

With the exception of the TS, the geometry optimizations were all carried out with each $-\text{CH}=\text{CH}_2$ group kept planar. Allowing the groups to become non-planar causes only small differences in the energy while greatly increasing the computer time necessary. The effects of the restriction will be discussed in a future publication. The length of the present paper also precludes details on the optimized geometries of the three species studied.

In addition to complete geometry optimization (with the above restriction) of the 1,3-butadiene structures at each critical point in the TPEC's obtained with the STO-3G, 3-21G and 6-31G \times basis sets, the relative energies for each structure were also computed using the 6-21G, 6-31G and 6-31G $\times\!\times$ basis sets. The results, given in Table 1, show that except for the STO-3G energy for the cis rotamer the energy differences are remarkably constant. The energies of the TS, gauche and cis structures all increase with increasing basis set size. This effect is also observed to carry over to the complete optimization with the 6-31G \times basis. Indeed the relative energies obtained with the 6-31G \times //3-21G computations are within several tenths of a kJ of those obtained in the optimizations.

It is therefore concluded that the structure of the second stable rotamer of 1,3-butadiene is gauche rather than cis, as predicted by the STO-3G optimizations. It must be pointed out that a cisoid form of 1,3-butadiene was trapped at low temperature (30 K) recently by Squillcote et al (ref.6). They concluded that the high energy form of 1,3-butadiene is cis planar but "a small twist angle (say, $<15^\circ$) would fit the data." The present computations predict a larger angle, around 38° (relaxing the $-\text{CH}=\text{CH}_2$ groups only reduces the angle to 35°). The STO-3G basis also predicted a trans - cis equilibrium in vinylcyclopropane whereas the 3-21G basis led to a trans - gauche ($\theta = 58.8^\circ$)(ref.3) equilibrium. The latter data is in excellent agreement with recent electron diffraction data on vinylcyclopropane (ref.7).

TABLE 1. RELATIVE ENERGIES (KJoules/mol) FOR 1,3-BUTADIENE BASIS2//BASIS1 COMPUTATIONS. BASIS1 WAS USED FOR THE GEOMETRY OPTIMIZATION AND BASIS2 TO COMPUTE THE ENERGY.

CONFORMER (θ°)	BASIS1	BASIS2					
		STO-3G	3-21G	6-21G	6-31G	6-31GX	6-31GXX
TRANS (180)	STO-3G	0	0	0	0	0	0
	3-21G	0	0	0	0	0	0
	6-31GX	-	-	-	-	0	-
TS (94.5) (101.8) (101.5)	STO-3G	23.52	23.32	23.94	25.58	25.03	24.99
	3-21G	23.10	23.65	24.32	26.05	25.58	25.53
	6-31GX	-	-	-	-	25.44	-
GAUCHE (38.1) ^a (38.5) ^a	3-21G	20.20	11.93	11.90	12.84	13.31	13.19
	6-31GX	-	-	-	-	13.23	-
	STO-3G	7.68	14.17	14.17	14.54	16.05	16.01
CIS (3)	3-21G	7.25	14.49	14.48	14.79	16.35	16.31
	6-31GX	-	-	-	-	16.26	-

^a Computed using the restriction that the $-\text{CH}=\text{CH}_2$ groups remain planar. The STO-3G optimization do not give a minimum at the gauche position. However, since the STO-3G//3-21G computation gives a lower energy for the gauche than for the cis structures, it is probable that using the gauche optimized STO-3G geometry for computations with the other basis sets would give a minimum. The problem would be the following : "Which value of θ should be used?"

Acrolein

The geometry of the trans conformer of acrolein was optimized first with both the STO-3G and 3-21G basis sets. TPEC's generated with the trans-optimized geometry, within the rigid rotor approximation only revealed a second minimum at the cis position with a TS near 90°. The geometries of the cis and TS structures were optimized. The results are, to say the least surprising, since the cis and trans conformers are predicted to be about 2 kJ apart by the STO-3G computations and only 5 J apart by the 3-21G optimizations. Much larger energy differences have been reported in the literature ($660 \pm 40 \text{ cm}^{-1}$) with the trans conformation being the more stable one (ref.8). Optimizations of the acrolein structures with the polarized 6-31G* basis are currently in progress in an attempt to verify this discrepancy. The TS is predicted to be at $\theta = 88.2^\circ$ (STO-3G) or $\theta = 91.6^\circ$ (3-21G) with the barrier heights to rotation from the trans position being 22.4 and 37.1 kJ/mol, resp.

Glyoxal

The geometries of the trans, TS and cis structures of glyoxal were optimized completely using the STO-3G, 3-21G and 6-31G* basis sets. Some of the geometrical features have already been compared with those from cyclopropanecarboxaldehyde and acetaldehyde (ref.4). The trans conformer is found to be most stable in all cases, in agreement with earlier theoretical studies (ref.9). The position of the TS is found to be closer to the cis conformation ($\theta = 87.9, 78.7$ and 73.0° for the STO-3G, 3-21G and 6-31G* basis sets, resp.). These latter values are in good agreement with that, $\theta = 74.7^\circ$, found by Osamura and Schaefer (ref.9) using a double zeta plus polarization basis set. The barrier to rotation from the trans position, in sharp contrast to 1,3-butadiene, is very basis set dependent. The STO-3G, 3-21G and 6-31G* barriers are 18.3, 41.1 and 30.0 kJ/mol, resp. Osamura and Schaefer (ref.9) reported a value of 6.8 kcal/mol (28.45 kJ/mol) and it thus appears that the effect of added polarization functions is important in oxygen containing species. The difference in energy between the trans and cis conformations increases with increasing basis set size being only 6.3 kJ/mol for the minimal basis. It 21.5, 23.5 and 24.5 for the 3-21G, 6-31G* and Osamura and Schaefer basis sets, resp. The experimental energy difference, reported by Currie and Ramsay (ref. 10) is 3.2 kcal/mol (13.4 kJ/mol), which is considerably less than

obtained with the more reliable basis sets used in this study or by Osamura and Schaefer. They have discussed this discrepancy and the reader is referred to their paper (ref.9).

The 3-21G basis set has been observed to give quite good results in computations on the acetaldehyde ground and excited states (ref. 11) and also for cyclopropanecarboxaldehyde ground state (ref.4). Nevertheless, the barrier heights to rotation from the cis-cyclopropanecarboxaldehyde conformation and the difference in relative energies of the cis and trans conformers was found to be decreased by geometry optimization with the 6-31G* basis or by 6-31G*/3-21G computations compared to those obtained in the 3-21G basis optimizations (ref.4). The TPEC's obtained with the various basis sets for glyoxal are given in Figure 1 and may be compared with those for cyclopropanecarboxaldehyde given in ref.4.

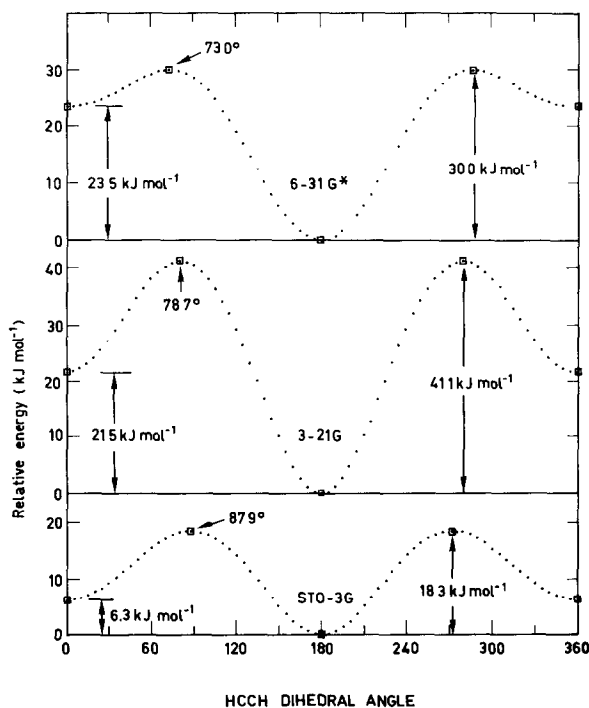


Fig. 1. Relative energies for rotation around the C - C single bond in glyoxal. The cis conformation corresponds to dihedral angles of 0 and 360°, the trans conformation to 180°.

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