An Ab Initio Structural and Vibrational Analysis of gauche,Trans,trans- and gauche,Cis,trans-Hexa-1,3,5-trienes†

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The results of complete geometry optimizations of the high energy stable gauche,Trans,trans- and gauche,Cis,trans- rotamers of hexa-1,3,5-trienes are reported at the RHF/6-31G//RHF/6-31G level. The angles of rotation around one of the single C—C bonds are found to be 33.7° and 45.5°, respectively. The corresponding harmonic force fields of these molecules are also reported at this level and corrected using scale factors transferred from buta-1,3-diene. A special scale factor was used for the central C=C double bond stretching coordinate to take into account vibronic coupling. The theoretical vibrational frequencies, calculated with the scaled quantum mechanical (SQM) force fields, allow a complete interpretation of the experimental vibrational spectra of these molecules.

INTRODUCTION

Recently published experimental investigations [1–5] of the vibrational spectra of trans,Trans,trans-(t,T,t-) and trans,Cis,trans- (t,C,t-) hexa-1,3,5-triene (Figure 1) have corroborated, in general, the results found using the empirical least squares method [5], the predictions from semiempirical QCFF/PI [4], PPP-CI [6,7], and CNDO/2 [8] computations, as well as the predictions from ab initio RHF/4-21G [9], RHF/6-31G [3,10], RHF/DZ + P [11], TZ + P [11], and CI-SD [12] models. The theoretical analysis of the experimental vibrational spectra [3–11] and the calculation of the geometrical parameters [3,4,9–17] clearly demonstrated that these structures are planar.

During the past decade, however, investigations of the structures and vibrational spectra of conjugated systems have centered on the high energy stable rotamers of these molecules. Indeed, for the first member of the polyene series, as well as for its 2-methyl and 2,3-dimethyl derivatives, the experimental vibrational frequencies of their high energy stable rotamers have been detected [18–24]. Ab initio theoretical analyses of the structures and the vibrational spectra of these rotamers have been performed at the RHF/6-31G//RHF/6-31G level [25–28]. Their structures have also been computed at the MP2/6-31G* level [28,29]. The systematic application of the same theoretical method throughout has made it possible to discover significant regularities in the structures and spectra of the high energy rotamers of buta-1,3-diene,
isoprene, and 2,3-dimethylbuta-1,3-diene [28]. Applying the same method to the high energy rotamers of \(t,T,t\) and \(t,C,t\)-hexa-1,3,5-triene allows one to obtain tentative geometrical parameters, in particular those concerned with the degree of twisting of the \(\text{H}_2\text{C}==\text{CH}==\) moieties [30]. A previous ab initio analysis of the vibrational spectra of these rotamers [3] was performed using a separate set of scale factors (empirical corrections for the corresponding force fields) that are different from the scale factors of buta-1,3-diene. Furthermore, this analysis [3] was carried out without taking into account the very important peculiarities of the vibrational spectra of this molecular class, that is, vibronic coupling.

In this connection it is of interest to predict theoretically the angles of internal rotation and the vibrational spectra of the high energy stable rotamers of the next member of this molecular series, hexa-1,3,5-triene. The experimental vibrational frequencies of the high energy rotamers of \(t,T,t\) and \(t,C,t\)-hexa-1,3,5-triene, measured in Refs. [31] and [32], also prompted us to perform the present work.

### COMPUTATIONAL DETAILS

Complete geometry optimizations of the high energy rotamers of \(g,T,t\) and \(g,C,t\)-hexatrienes were performed at the RHF/6-31G level [33] using the Gaussian 82 [34] and Gaussian 86 [35] programs. The optimized