



Microwave study of internal rotation in *para*-tolualdehyde: Local versus global symmetry effects at the methyl-rotor site

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ABSTRACT

The rotational spectrum of *para*-tolualdehyde ($\text{CH}_3\text{-C}_6\text{H}_4\text{-CHO}$) has been measured using three different microwave spectrometers, with the goal of quantifying the influence of the aldehyde group at the top of the benzene ring on the internal rotation barrier seen by the methyl group at the bottom of the ring. This barrier consists of a six-fold component, which results from the local C_{2v} symmetry of the benzene ring seen by the methyl top (as in toluene), and an additional three-fold component, which results from information on the non- C_{2v} symmetry at the aldehyde site at the top of the ring being transmitted to the methyl-group site at the bottom of the ring. The nearly-free internal rotation of the methyl group splits each of the rotational transitions into two components, one of A and one of E symmetry. Assignment and fit of 786 A-state and E-state transitions to an internal rotation Hamiltonian containing barrier terms of three-fold ($V_3 = 28.111(1) \text{ cm}^{-1}$) and six-fold ($V_6 = -4.768(7) \text{ cm}^{-1}$) symmetry with respect to the internal rotation angle, as well as the three rotational constants and a number of higher-order torsion-rotation interaction terms, resulted in residuals equal to experimental measurement uncertainty. Isotopic data from all eight mono-substituted ^{13}C species and the one ^{18}O species were obtained in natural abundance and used to determine an r_s substitution structure. Various chemical and physical implications of this structure and the two barrier parameters are discussed.

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1. Introduction

Large effects on internal rotation barriers caused by changes in neighboring aromatic π -electron systems in the molecule were investigated experimentally some time ago in a pioneering series of papers from the Tohoku University group [1–7]. They showed (among other things) that the height and phase of the three-fold barrier in a number of *ortho*, *meta*, and *para* substituted toluenes change dramatically upon going from the ground electronic state either to the first excited electronic state of the neutral ($S_1 \leftarrow S_0$) or to the ground state of the ion ($C_0 \leftarrow S_0$). These experimental results quickly led to theoretical discussions of how changes in the π -electron system might affect methyl rotor barriers [8–11].

It was in this context that we began (some time ago [12]) a study of the three-fold and six-fold contributions to the internal

rotation barrier in the ground-state of *p*-tolualdehyde (pTA). The structure of this molecule ($\text{CH}_3\text{-C}_6\text{H}_4\text{-CHO}$, see Fig. 1) offers a good model for comparing the magnitude of steric effects with the magnitude of electronic structure effects on internal rotation barriers. While the present work was in progress, a study of the closely related molecule trifluoro-*p*-tolualdehyde ($\text{CF}_3\text{-C}_6\text{H}_4\text{-CHO}$) was carried out [13]. Since the present microwave study does not involve changing the electronic state, we must derive information by comparing the three-fold and six-fold internal rotation barriers in pTA with those in chemically related molecules. To obtain both the three-fold and six-fold terms in the barrier expansion from experimental splittings, it is necessary to study torsional excited states, which for pTA lie above the top of the barrier. Rotational levels in such excited states are somewhat complicated.

Section 2 describes the new measurements that form our experimental data set. Section 3 presents our final spectral fit (carried out with the BELGI-Cs program [14,15]). Section 4 presents our isotopic substitution structures. In Section 5 we show that our initial chemically intuitive ideas concerning pTA are not consistent

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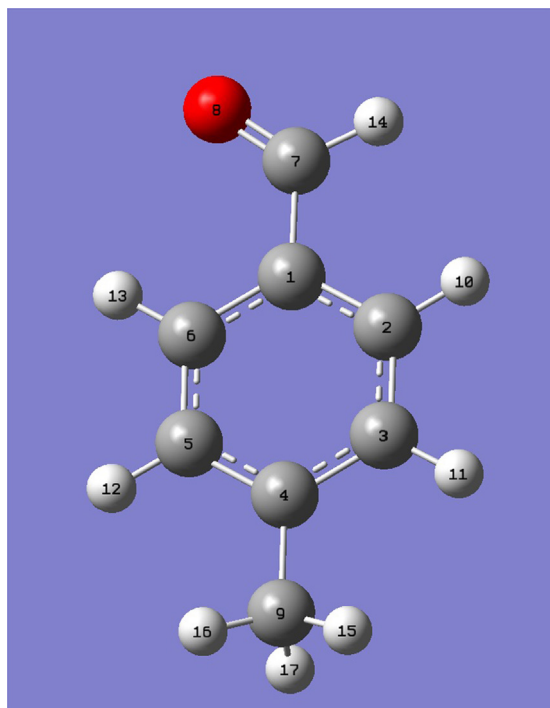


Fig. 1. Structure of p-tolualdehyde, drawn nearly to scale, with an aldehyde group at the top of the benzene ring and a methyl group at the bottom. Atom numbering is that used in the text.

with the substitution structure. In Section 6, we discuss the torsional potential constants V_3 and V_6 . Section 7 presents brief conclusions. A qualitative overview of regularities and irregularities of the torsion-rotation levels of pTA, as calculated from our fitting constants, as well as details of the least-squares fit itself are given in the [supplemental material](#).

2. Measurements and data set

The data set here consists of Fourier transform microwave (FTMW) measurements in the cm-wave region and Stark-modulated absorption measurements in the mm-wave region, that were obtained in three different laboratories. It is convenient to recall the following facts. (i) Rotational levels and the transitions of one-top internal rotor molecules can be classified as being of A_1 , A_2 , or E species in the permutation-inversion (PI) group G_6 . (ii) For the low-barrier case found in pTA, the free-rotor quantum number m , corresponding to torsional levels of approximate energy Fm^2 , is more useful than the harmonic-oscillator vibrational quantum number $\nu_{torsion}$ (abbreviated below as ν_t). (iii) Torsional symmetry species are determined by the m quantum number, with $m = 0, \pm 1, \pm 2$, and ± 3 corresponding to levels of symmetry species A_1 , E, E, and $A_1 \oplus A_2$ in G_6 , respectively. (iv) In pulsed molecular beams at temperatures of a few kelvin, A levels relax to A, and E levels relax to E, so only levels with $|m| = 0$ and 1 are significantly populated in the NIST and Hannover molecular beam measurements.

2.1. NIST measurements

Measurements with the NIST FTMW spectrometer, which operates from 8 to 26.5 GHz [16], were begun almost two decades ago, but were soon abandoned because all attempts to alter nozzle conditions to permit observation of levels from excited torsional states with $|m| = 2$ or 3 (and thus to determine independently V_3 and V_6) failed. Almost 180 of these measurements remain in the

presently fitted data set, however, with estimated measurement uncertainty of 1 kHz.

2.2. Hannover measurements

A number of new lines were measured with the Hannover FTMW spectrometer [17] in the range from 4.7 to 19 GHz. In addition, a number of the NIST lines were remeasured with greater accuracy. About 125 such lines are in the fit, with estimated measurement uncertainty of 0.5 kHz. Even with the greater sensitivity available with the Hannover spectrometer, however, all attempts to observe transitions involving torsional levels with $|m| > 1$ also failed.

2.3. Bologna measurements

The breakthrough (from the point of view of this project) came when mm-wave measurements were carried out with the Bologna free-jet absorption spectrometer [18,19], which operates in the range from 50 to 80 GHz. Line densities in these Bologna measurements strongly suggested that transitions involving excited torsional levels were present in the spectral recordings. After repairing five non-functioning heaters (out of six) in the diffusion pump that was temporarily in use for the preliminary measurements, the desired transitions disappeared. They reappeared only when the gate valve of the repaired pump was “nearly closed.” All excited torsional state measurements were made with this reduced-pumping-speed configuration, which (from visual inspection of relative intensities) we estimate raised the rotational temperature in the beam to about 30 K. Assigned measurement uncertainties for all Bologna measurements are 70 kHz. Since the Bologna spectrometer uses Stark modulation, excited-torsional-state transitions involving low K_a values, with slow Stark effects, often became too weak to observe [20].

3. Analysis and spectral fits

Assignment was begun in the usual way, i.e., a subset of A species transitions was first fit to an asymmetric rotor Hamiltonian. Next, the XIAM program [21] was used to get a rough fit of the A and E transitions together. Finally, the BELGI-Cs program [14,15] was used to obtain a global fit with observed-minus-calculated (obs-calc) residuals comparable to experimental error.

The assignment and fitting procedure for the FTMW data was almost as simple as outlined in the previous paragraph, but the same was not true for the mm-wave spectra, essentially because of the much denser spectrum caused by the presence of (the desired) transitions within the thermally hot $|m| = 2$ and 3 manifolds. Calculations indicate that $|m| = 2$ and 3 levels are from 40 K to 70 K above the lowest $|m| = 1$ and 0 levels with the same E or A torsional species, which causes transitions involving them to be significantly weaker than those within the $|m| = 0$ and 1 manifolds. Also, the K structure of rotational levels within the $|m| = 2$ and 3 manifolds is much more irregular than the K structure of levels in the $|m| = 0$ and 1 manifolds (see [supplemental material](#)). Consequently, a fairly large number of trial-and-error iterative cycles of the type: assignment guesses \rightarrow fits with guessed parameter sets \rightarrow more assignments, etc. had to be carried out before arriving at the final fit presented in this paper.

An overview of our global fit is shown in Table 1. The Hannover and NIST FTMW lines are fit to 0.6 kHz and 0.9 kHz, respectively, which is quite satisfactory. The Bologna mm-wave absorption lines are fit to 69 kHz, which is also quite satisfactory, in view of their weakness and frequent blending.

The parameters from the fit are shown in Table 2. From the point of view of total number of parameters required, the situation

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