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TECHNICAL REPORT #30


"TORSIONAL MOTION IN AROMATIC MOLECULES -

XYLENES AND N-PROPYL TOLUENES"


by


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## ABSTRACT

Supersonic molecular jet spectroscopy is used to obtain information on the torsional motion in methyl, ethyl and n-propyl substituted benzenes. Dispersed emission and time of flight mass spectral results are evaluated for toluene, the three xylenes, 1,3-diethylbenzene and 3-n-propyltoluene. The aromatic ring methyl groups in m- and p-xylene can be considered as independent free rotors in $S_0$ and $S_1$ while in o-xylene they are considerably more hindered in these two states and for $S_1$ cross kinetic and potential terms must be introduced. The two conformations of 1,3-diethylbenzene (syn and anti, with the ethyl groups perpendicular to the plane of the benzene ring) and the three conformations of the propyl group in 3-n-propyltoluene (anti, syn-gauche and anti-gauche) are observed.

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To an ever increasing extent, information regarding torsional vibrations of organic molecules is being provided by theoretical treatments rather than by experimental observation.[1] When experimental data are available, all too frequently they pertain to mole fraction-weighted averages of the individual contributing conformations rather than the individual conformations themselves.[2] We now demonstrate that supersonic molecular jet spectroscopy can provide a novel means (a) to determine experimental values for torsional potential barriers in $S_o$ and $S_1$, (b) to "freeze out" molecular conformations which have very low (ca. 1-5 kcal $mol^{-1}$) free energy barriers between themselves, (c) to "count" the number of stable ground state conformations, and by doing so, establish their molecular geometries, and (d) to observe spectroscopic properties of these individual conformations.

Much current interest exists in the conformational analysis of alkyl-substituted benzene substrates, and herein we focus specific attention on the first three members of this class of compound: methyl, ethyl, and n-propyl. Both time of flight mass spectra (TOFMS) and dispersed emission (DE) spectra are determined for the systems studied.[3] Figure 1 presents the TOFMS of m-xylene for the $0_o^o$ region of the $S_1 \leftarrow S_o$ transition. The various features of this spectrum are attributed to transitions between internal rotor states of the two methyl groups. A double 1-dimensional rigid rotor model can be employed to fit these data.[4-6] Parameters of this quantum mechanical model can be found for both the ground $(S_o)$ and excited $(S_1)$ states and are reported in Table 1 for m-xylene and the other compounds discussed herein.

The TOFMS and DE spectra of o-xylene are considerably different from those of m-xylene. The methyl groups of o-xylene act as independent hindered rigid rotors in the $S_o$ state,[7] whereas both kinetic and potential

interactions between the two neighboring groups can be identified in the $S_2$ state. The relevant rigid rotor model parameters for $S_o$ and $S_1$ states are presented and compared with those for other systems in Table 1.

For $\underline{n}$-alkylbenzenes, $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta)$ is the first torsional angle which defines the orientation of the alkyl group relative to the aromatic ring (c.f. $\underline{3}$). Ethylbenzene ($\underline{4}$) is the prototypical example, with a barrier to rotation[2] about $\tau_1$ of <5 kcal mol$^{-1}$. While some recent theoretical and experimental studies have concluded that the orthogonal conformation is preferred for $\underline{4}$, some controversy remains and a number of reports conflict with this assignment.[8] The TOFMS and DE spectra of 1,3-diethylbenzene ($\underline{5}$) reveal $\underline{two}$ origins, one each for the syn and anti orthogonal conformations, $\underline{5s}$ and $\underline{5a}$ respectively. Had planar ($\tau_1=0$) or angular conformations ($0<\tau_1<90°$) been obtained, then more than two origins for $\underline{5}$ would have been observed. Importantly, the TOFMS experiment is sufficiently sensitive to molecular symmetry to distinguish between $\underline{5s}$ and $\underline{5a}$.



$\underline{3}$          $\underline{5s}$          $\underline{5a}$
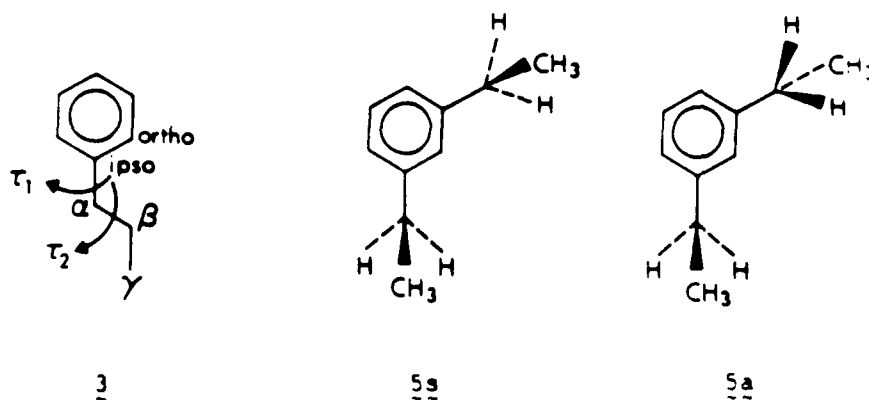
$\underline{n}$-Propylbenzene ($\underline{6}$) serves as the prototypical example to define the second torsional angle $\tau_2$ (c.f. $\underline{3}$). In their pioneering report, Hopkins, Powers and Smalley had observed two origins in the TOFMS for $\underline{6}$ but could not distinguish between the possible (anti, gauche, or eclipsed) conformations.[3] Over the last few years, evidence has accumulated from detailed studies of

and related compounds that $CH \cdots \pi$ attractive interactions can stabilize conformations when appropriate molecular geometries are possible.[10] Most studies have assumed that anti and gauche conformations are predominant,[11] and this assumption has been found to be consistent with empirical force field (EFF) calculations;[10] however, EFF calculations are not specifically parameterized for $CH \cdots \pi$ interactions. Indeed, Hopkins, Powers and Smalley[9] suggested that the eclipsed form could be the preferred conformation for n-propylbenzene, pending unambiguous experimental data.

Figure 2 shows the TOFMS of 3-n-propyltoluene (7). Three origin transitions, appearing as doublets, are observed. These correspond to the anti conformation 8 and the two gauche conformations, syn-gauche 9s and anti-gauche 9a. Had the eclipsed conformation 10 and the anti conformation 8 been predominant to the exclusion of the gauche conformations, only two origin transitions would have appeared. The doubling of the origins is due to two non-equilibrating methyl rotor states of 8, namely the 0a and 1e states. The doublets at ca. 25 $cm^{-1}$ from each origin are due to propyl torsions, features also noted in the spectra of n-propylbenzene and 4-n-propyltoluene. The observation of only three origins also substantiates the conclusion derived from the data on the ethylbenzenes that $\tau = 90°$.



9s, $R_1$ = H, $R_2$ = $CH_3$

9a, $R_1$ = $CH_3$, $R_2$ = H
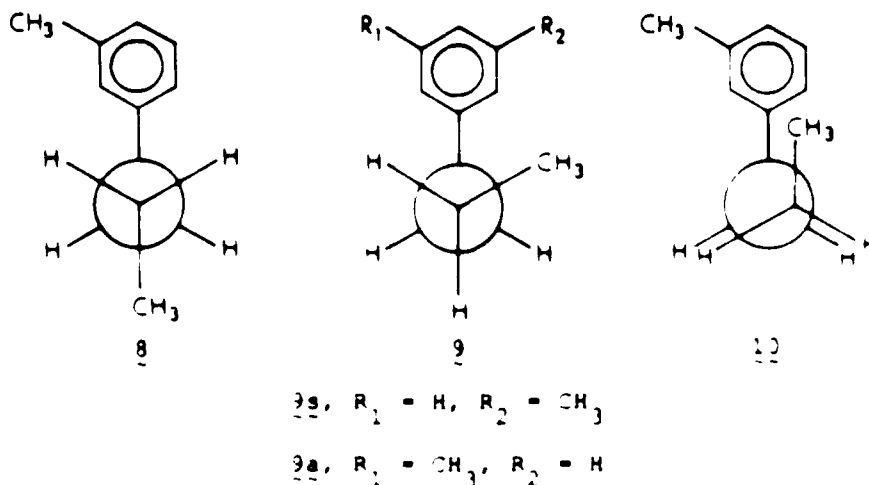
These results show:  a) supersonic molecular jet spectroscopy is capable of observing specific molecular conformations which have very low barriers to conformational interchange; b) aromatic ring methyl groups in the p-, and m-xylenes can be considered as independent, nearly free rotors in $S_0$ and $S_1$; c) the aromatic ring methyl groups in o-xylene are considerably more hindered in $S_0$ and $S_1$, and for $S_1$, cross kinetic and potential terms must be introduced; d) the barriers for rotation are greater in $S_1$ than $S_0$; e) the dynamic nature of the motion of the ring methyl groups is contrasted by a more static, locked-in character of the aromatic ethyl and n-propyl substituents;  f) aromatic n-alkyl substituents have their first C-C torsion perpendicular to the plane of the aromatic ring; and g) aromatic n-propyl substituents exist in anti and gauche conformations, as observed in these TOFMS/DE experiments.

## TABLE I

Summary of the Hamiltonian parameters used to fit the
experimental data for the alkylbenzenes.
Values are given in cm$^{-1}$[a]

| | $S_0$ | | $S_1$ | | | |
|---|---|---|---|---|---|---|
| | $V_3$ | $V_6$ | $V_3$ | $V_6$ | $\chi_6$[b] | $V'_3$[c] |
| toluene | 0 | 10 | 0 | 25 | - | - |
| p-xylene | 0 | 10 | 0 | 25 | - | - |
| m-xylene | 0 | 25 | 81 | -30 | - | - |
| o-xylene | 425 | 18 | 166 | 0 | .72 | -25 |
| 3-n-propyltoluene | 0 | 23 | 75 | 0 | - | - |

[a] 1 kcal mol$^{-1}$ = 350 cm$^{-1}$.  [b] Kinetic cross term.  [c] Potential cross term.

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FIGURE CAPTIONS


FIGURE 1   Electronic absorption spectrum of the $O_0^0$ region of m-xylene,

obtained with time-of-flight mass detection (TOFMS). The origin

occurs at 36956.3 $cm^{-1}$. The two features at 3.7 and 7.0 $cm^{-1}$ to

lower energy of the origin are due to methyl torsions, and their

positions are indicative of differences in the potential barrier

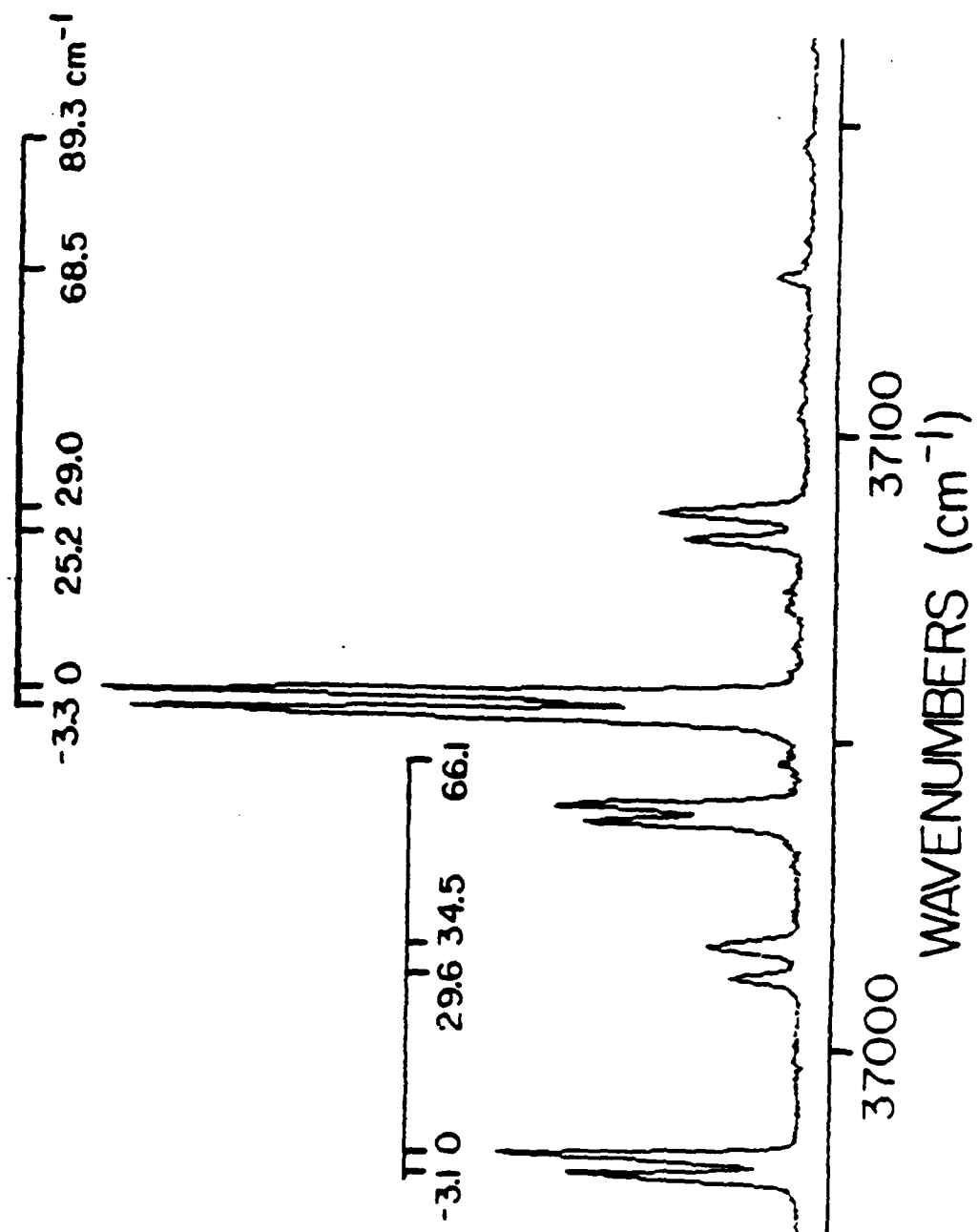to methyl rotation in $S_0$ and $S_1$.


FIGURE 2   Electronic absorption spectrum (TOFMS) of the $O_0^0$ region of 3-n-

propyltoluene. The spectrum contains three origins at 36982.8,

37040.4 and 37060.1 $cm^{-1}$, corresponding to three different propyl

group conformations. Accompanying each origin peak is a second

peak to lower energy which is assigned as due to a methyl

torsion. The doublet structures are indicative of differences in

the potential barrier height to methyl rotation in $S_1$ and $S_0$.

-7.0 0   16.9   32.6
  -3.7          29.0

70.2   87.5
  75.2    91.3

164.4 169.0
    cm⁻¹

37000

37100
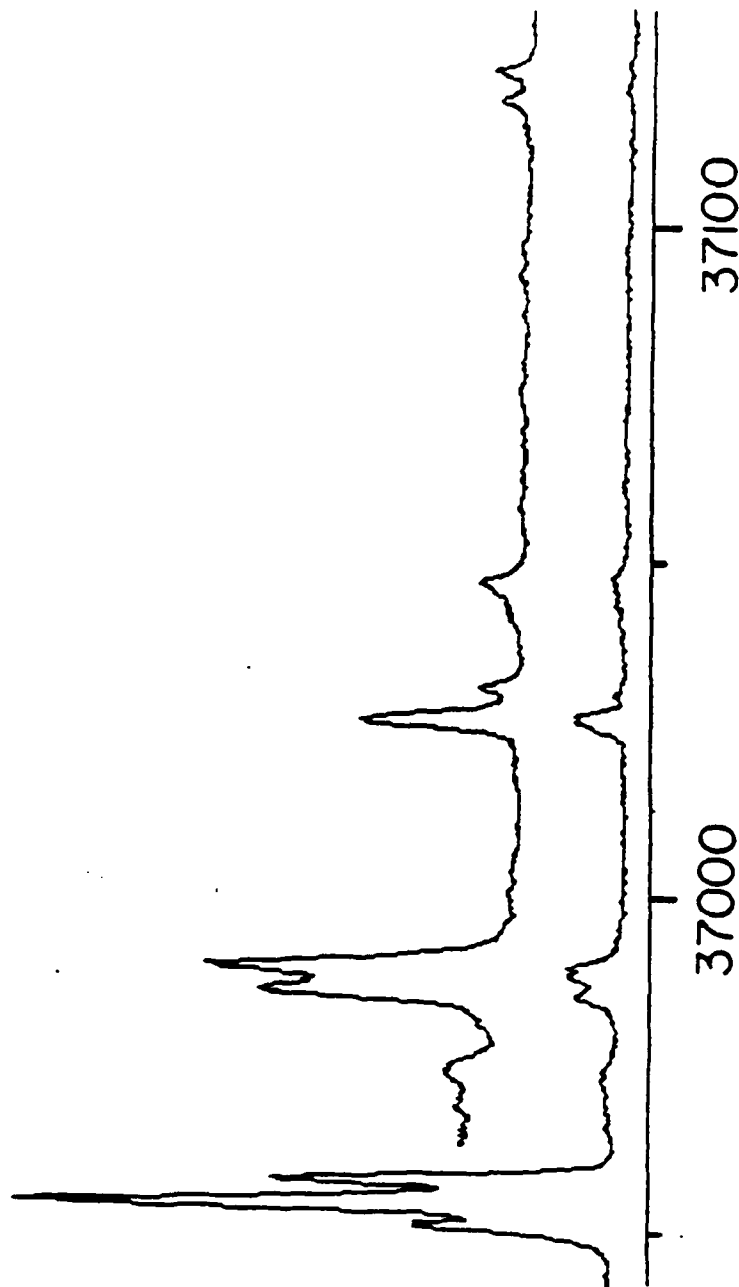
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