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Supersonic molecular jet spectroscopy of ethylbenzene, the ethyltoluenes, and the diethylbenzenes

P. J. Breen and E. R. Bernstein
Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523
Jeffrey I. Seeman
Philip Morris U. S. A. Research Center, P. O. Box 26583, Richmond, Virginia 23261

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Time-of-flight mass spectra are presented for the $S_1 \leftarrow S_0$ origin region of jet-cooled 1,2-, 1,3-, and 1,4-diethylbenzene, and 2-, 3-, and 4-ethyltoluene. The spectra for the diethylbenzenes exhibit two origins which are assigned to *syn* and *anti* conformations of the ethyl groups relative to the aromatic ring. The existence of two origins in the 1,3-diethylbenzene spectrum, and only one in the 3-ethyltoluene spectrum, strongly implies that the stable orientation of the ethyl groups is with the β-carbon atom of the ethyl group projecting perpendicular to the plane of the aromatic ring. The size and shape of the potential barrier to rotation of the ring methyl group is obtained by treating the methyl group as a one-dimensional rigid rotor and fitting the calculated energy levels to observed features in the spectra. The results (for the para isomer $B = 5.20\ \text{cm}^{-1}$, $V_6 = 31.00\ \text{cm}^{-1}$; for the meta isomer, $B = 5.40\ \text{cm}^{-1}$, $V_3 = 78.00\ \text{cm}^{-1}$; and for the ortho isomer, $B = 5.50\ \text{cm}^{-1}$, $V_3 = 89.00\ \text{cm}^{-1}$) indicate that the methyl group experiences an increased barrier to rotation in the order para < meta < ortho isomer.

I. INTRODUCTION

The orientation and rotational energy properties of substituents on aromatic rings are topics of much current and fundamental interest.[1-4] The related structures **1** and **2** generalize a set of compounds in which the atom directly attached to the aromatic ring has one heavy atom and either hydrogens or lone pairs of electrons bonded to it.

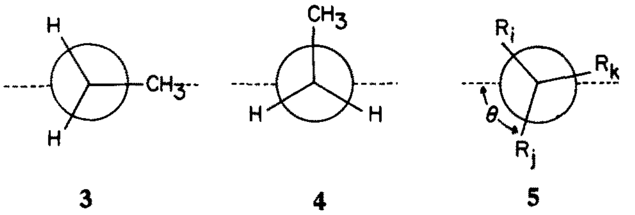
Ar-X-alkyl Ar-CH_2-Y

1 **2**

X = CH_2,O,S,NH,etc. Y = OH,CH_2alkyl,NH_2,X,etc.

As shown in scheme I for ethylbenzene, a variety of distinct conformations are available to **1** and **2**: the heavy atom in the plane of the aromatic ring (cf. **3**), perpendicular to the ring (cf. **4**), or at some other angle with respect to the ring (cf. **5**).[5] Distinguishing among these alternatives and deriving internal rotational potentials are typically quite challenging tasks, even with the most advanced spectroscopic and theoretical methodologies.[1-5]

Scheme I



3 **4** **5**

$R_i = CH_3$, $R_j = R_k = H$

$(0° < \theta < 90°)$

Specifically, the orientation of the ethyl group in ethyl-substituted aromatic molecules such as ethylbenzene is in some dispute. While the most recent work indicates that the methyl group in ethylbenzene is perpendicular to the plane of the benzene ring as in **4**,[6,7] a variety of other experimental studies have suggested skew (**5**), eclipsed (**3**), or even mixtures of these conformations.[8]

In this paper[9] we examine two classes of compounds, the diethylbenzenes and the ethyltoluenes, employing supersonic molecular jet spectroscopy of their respective $S_1 \leftarrow S_0$ origin bands. We can thereby observe the individual stable conformations that occur for an ethyl group substituted onto an aromatic ring. The effects of substitution pattern (ortho, meta, and para) on the energy of the transitions and on the conformations exhibited by the molecules will also be discussed. The work on the ethyltoluenes is an extension of previous studies done on the xylenes[10] and *n*-propyltoluenes.[11] In addition, this work helps lay the foundation for future conformational studies on more complex organic molecules.

II. EXPERIMENTAL PROCEDURES

All supersonic molecular jet spectra are obtained using one-color two-photon ionization with time-of-flight mass detection. The time-of-flight mass spectrometer (TOFMS) chamber is as described elsewhere.[12] A pulsed molecular jet is employed using an R. M. Jordan pulsed valve. Although in most cases, 100 psig He is used as the carrier gas, occasionally various percentages of Ar in He are used to achieve better cooling, as specified. All experiments are carried out with the samples at room temperature.

Empirical force field (FFF) calculations are performed for the diethylbenzenes using the molecular orbital–molecular mechanics (MOMM-85) algorithm of Kao *et al.*[13] MOMM-85 has been specifically parametrized for aromatic ring systems and is known to reproduce experimental geometries and energies. These ground state calculations are performed using complete geometry optimization. The steric energy and potential energy barriers to rotation as a function of angular displacement about the C_{aromatic}–C_α bond (i.e., the torsion angle defined by the C_{ortho}–C_{ipso}–C_α–C_β bonds) are thus estimated.

III. RESULTS

A. Ethylbenzene

Before considering the diethylbenzenes and ethyltoluenes, the TOFMS of ethylbenzene itself is useful to examine: the spectrum is presented in Fig. 1. The spectrum contains a single origin at 37 587.8 cm^{-1}, with weaker features at 28.6 and 98.0 cm^{-1} to higher energy of the origin. These weak features are presumably due to torsions of the ethyl group, and are similar to features observed in the TOFMS of *n*-propylbenzene.[11,14]

B. 1,4-Diethylbenzene

The TOFMS of jet-cooled 1,4-diethylbenzene using 2% Ar in He as the expansion mixture is displayed in Fig. 2. The spectrum presents two intense features, at 37 008.9 and 37 013.0 cm^{-1}, presumably corresponding to origins of two distinct conformations of the molecule: one in which both ethyl groups project up on the same side of the ring (*syn*) and one in which the two ethyl groups project up and down on opposite sides of the ring (*anti*). This assignment will be discussed in more detail in the next section. The remaining weak features to higher energy of the two origins in Fig. 2 are assigned as due to torsions of the ethyl chains. Using the MOMM-85 algorithm,[13] two energy minima are found corresponding to the *syn* and *anti* conformations. The heats of formation and steric energies of these conformations are shown in Table I.

C. 1,3-Diethylbenzene

The TOFMS of 1,3-diethylbenzene is present in Fig. 3. As for 1,4-diethylbenzene, two separate origins, belonging to *syn* and *anti* conformations of the two ethyl groups, are again observed at 37 156.1 and 37 165.1 cm^{-1}. Note, however, the increased separation between these two origins: 9.0 cm^{-1} for 1,3-diethylbenzene vs only 4.1 cm^{-1} for 1,4-diethylbenzene. This change in transition energy separation from 1,4- to 1,3-diethylbenzene is presumably indicative of the difference in proximity of the two ethyl groups in these molecules. Figure 3 also displays two weak features to the blue of the two origins which are assigned as due to ethyl torsions. Calculations for these molecules are presented in Table I.

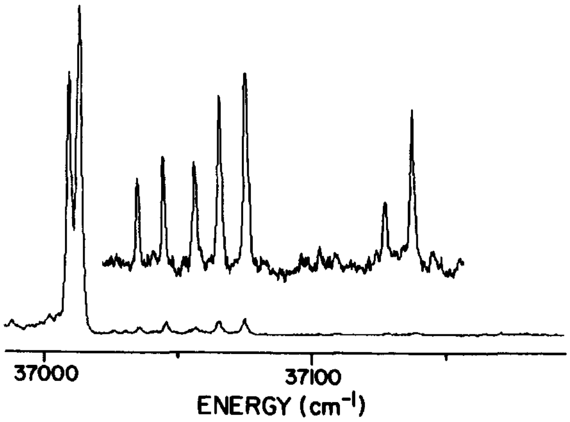


FIG. 2. One-color TOFMS of the 0_0^0 region of 1,4-diethylbenzene. Two different origins, separated by 4.1 cm^{-1}, are present in the spectrum, corresponding to *syn* and *anti* conformations of the ethyl groups. The remaining features in the spectrum are attributed to torsions of the ethyl group.

D. 1,2-Diethylbenzene

Figure 4 presents the TOFMS for jet-cooled 1,2-diethylbenzene. The spectrum consists of one intense origin feature at 37 151.3 cm^{-1} with a number of weaker features to the blue and one small feature to the red at 37 134.4 cm^{-1}. Since the spectra for the para and meta isomers evidence two origins, one for each of the two possible conformations in diethylbenzene, one suspects that this latter weak feature may be the other origin for 1,2-diethylbenzene. An alternative possi-

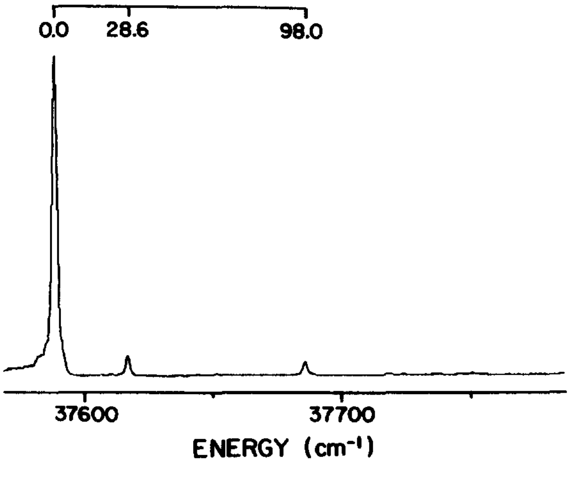


FIG. 1. One-color TOFMS of the 0_0^0 region of ethylbenzene. The weak features to higher energy of the origin are presumably due to torsions of the ethyl group.

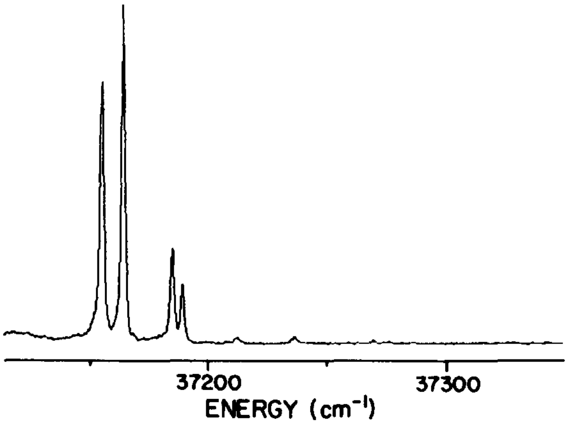


FIG. 3. One-color TOFMS of the 0_0^0 region of 1,3-diethylbenzene. The spectrum contains two different origins, separated by 9.0 cm^{-1}, arising from *syn* and *anti* conformations of the ethyl groups. The remaining features, to higher energy of the origins, are attributed to torsional motion of the ethyl groups.

TABLE I. MOMM-85 calculated heats of formation and steric energy in kcal/mol for minimum energy conformations of the diethylbenzenes.

	Conformations[a]			
	Anti	*Syn*	Other	
Compounds	Steric energy/heat of formation[b]			ΔH_f^0 (expt)
1,2-Diethylbenzene	− 4.43/18.43 [92.3°/92.4°]	− 3.72/19.09 [81.3°/ − 110.6°]	− 3.24/19.49 [95.5°/170.4°]	− 4.53
1,3-Diethylbenzene	− 5.61/17.43 [88.6°/88.6°]	− 5.63/17.41 [88.4°/ − 87.8°]	···	− 5.52
1,4-Diethylbenzene	− 5.60/17.45 [93.3°/94.9°]	− 5.61/17.44 [90.3°/ − 94.0°]	···	− 5.32

[a] The angles indicated [X°/Y°] define the orientation of the ethyl substituents. These two torsion angles refer to (C_{ortho}–C_{ipso}–$\underline{C}H_2$–$\underline{C}H_3$). The C_{ortho} atoms are chosen to be the ring carbon atom closer to the other ipso carbon atom, i.e., closer to the other ethyl substituent. For 1,4-diethylbenzene, the two chosen C_{ortho} are adjacent to each other.

[b] MOMM-85 calculated parameters, see Ref. 10.

[c] J. D. Cox and G. Pilcher, *Thermodynamics of Organic and Organometallic Compounds* (Academic, New York, 1970).

bility for the assignment of this feature is, of course, an ethyl chain torsion hot band. This latter possibility can be explored under expansion conditions which vary the pressure and expansion gas mixtures (e.g., 50–150 of psig, He, N_2, Ar, mixtures of these gases and CF_4/He mixtures). In all these cases, the features at 37 157.1 and 37 165.4 cm^{-1} disappear, strongly implying that they are hot bands, but the feature of concern at 37 134.4 cm^{-1} does not change its intensity relative to the origin. We therefore assign it to be a separate origin corresponding to the *syn*, sterically hindered conformation of the two ethyl groups. The steric interference between the two ethyl groups must make the *syn* conformation less energetically favorable than the *anti* conformation, resulting in its depopulation and the corresponding weak intensity displayed in Fig. 4. The energy difference between the two origins is 16.9 cm^{-1} for the ortho isomer, indicating a widening difference between the energy of the two molecular conformations through the series 1,4-, 1,3-, and 1,2-diethylbenzenes. Figure 5 illustrates the MOMM-85 calculated steric energy contour for rotation of the two ethyl groups in 1,2-diethylbenzene with respect to the aromatic ring in the vicinity of the three energy minima. The exact locations and energies of these three minima are listed in Table I.

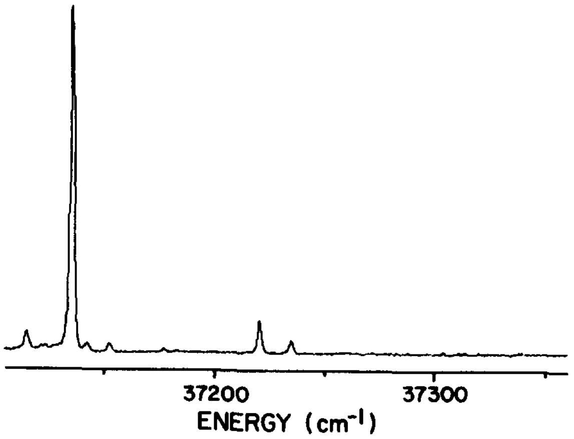


FIG. 4. One-color TOFMS of the 0_0^0 region of 1,2-diethylbenzene. The spectrum contains one intense origin, and another much weaker origin to lower energy of the intense feature. The latter assignment is based on cooling experiments which prove this feature is not a hot band. See the text for a more complete discussion of this feature.

E. 4-Ethyltoluene

The TOFMS of jet-cooled 4-ethyltoluene is presented in Fig. 6. The single intense feature at 36 890.6 cm^{-1} is assigned as the origin, and the weak features to the blue of it are assigned as a mix of ethyl and methyl torsions. The potential for methyl rotation in such a molecule can be characterized by treating the system as a one-dimensional rigid rotor and diagonalizing the Hamiltonian for the wave function expanded in terms of the one-dimensional rotor functions[15]: such an analysis has been carried out for the methyl groups of toluene,[10] the xylenes,[10] and the *n*-propyltoluenes.[11] A comparable analysis is repeated herein for 4-ethyltoluene. The potential barrier to methyl free rotation in this molecule can be thought of as arising from two sources: the benzene aromatic ring (a sixfold potential, V_6) and the perpendicular to the plane para-ethyl group (a threefold potential, V_3). The distance separating the ethyl and methyl substituents makes the latter contribution unlikely, and in fact, as is seen from the excellent fit illustrated in Table II for 4-ethyltoluene, no such V_3 contribution is necessary to fit the data. In addition, the depth of the sixfold potential is 31.0 cm^{-1}, a value which is consistent with the previously reported value of 24.0 cm^{-1} found for toluene in S_1.[10] The two methyl groups of *p*-xylene have potential barriers in S_1 identical to that for the methyl group of toluene.[10] The methyl rotor potential for toluene is also quite similar to that for the ring methyl group of *p*-*n*-propyltoluene.[11] The implication is that small alkyl groups which are substituted para to a methyl group have only a very small, if any, effect on the potential barrier to methyl rotation.

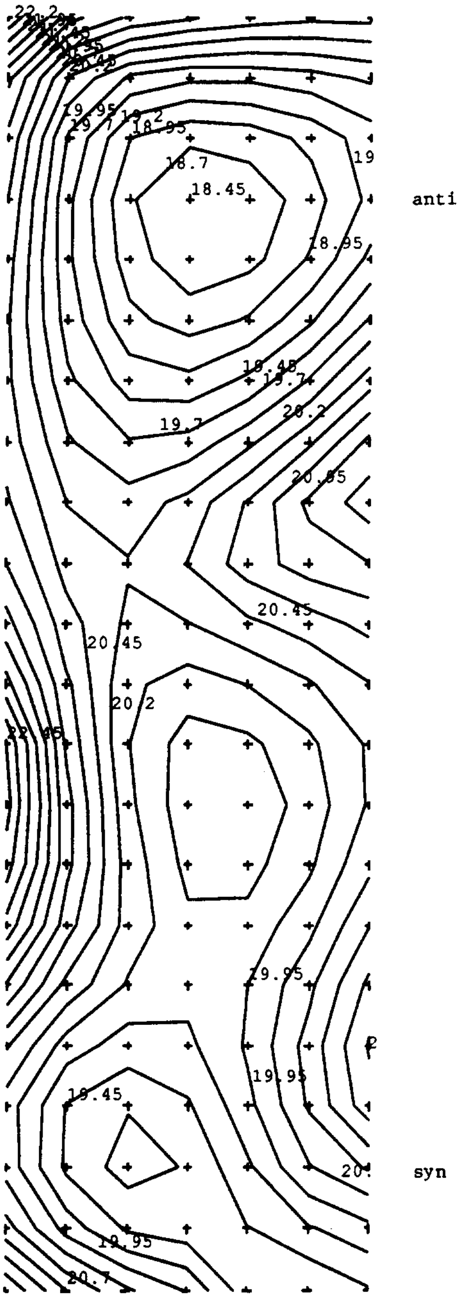


FIG. 5. MOMM-85 calculated steric energy (kcal/mol) contour for rotation of the two ethyl groups in 1,2-diethylbenzene with respect to the aromatic ring in the vicinity of the three energy minima (see Table I for values of these minima). The torsion angles are $\tau = \tau(C_2\text{–}C_1\text{–}C_7\text{–}C_8)$ and $\phi = \tau(C_1\text{–}C_2\text{–}C_9\text{–}C_{10})$. A positive sign for the torsion angle A–B–C–D indicates that when one views down the B–C bond, D is rotated clockwise from A.

Using a sixfold potential well, the fitted rotational constant for the ring methyl group of 4-ethyltoluene is 5.2 cm^{-1}, and the calculated methyl group zero point energy is 14.9 cm^{-1}.

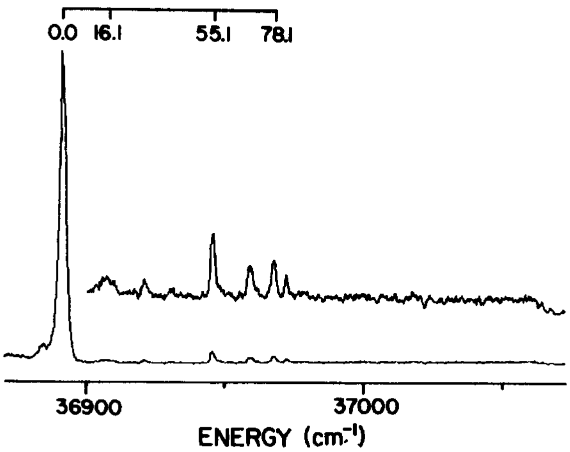


FIG. 6. One-color TOFMS of the 0_0^0 region of 4-ethyltoluene. The weak features to higher energy of the origin are due to both methyl group rotational and ethyl group torsional motions. Assignments of the methyl rotor features are given in Table I.

F. 3-Ethyltoluene

Figure 7 presents the TOFMS of jet-cooled 3-ethyltoluene. The most intense feature of the spectrum is a doublet with components at 37 050.6 and 37 054.0 cm^{-1} (3.4 cm^{-1} spacing). This type of doublet structure commonly occurs at the origin(s) in the TOFMS of meta-substituted alkyltoluenes, and has been observed, for example to occur in the TOFMS of *m*-xylene,[10] 3-*n*-propyltoluene,[11] 3-isopropyltoluene,[16] and 3-*t*-butyltoluene.[16] In the cases of *m*-xylene, 3-*n*-propyltoluene, and 3-*t*-butyltoluene, DE spectroscopy proves that the red components of these doublets, which are typically displaced ~3.5 cm^{-1} from the higher energy feature, are hot bands corresponding to the $1e \rightarrow 1e$ rotational transition of the ring methyl rotor. The blue, or higher-energy components of the doublets are the actual origins corresponding to a $0a_1 \rightarrow 0a_1$ methyl rotor transition.

Alkylbenzenes also tend to exhibit a weak feature in their respective TOFMS at or near 30 cm^{-1} to higher energy of the origin. This feature is presumably due to torsional motion of the alkyl group, and has been observed in the TOFMS of, for example, ethylbenzene (Fig. 1), *n*-propylbenzene,[11] isopropylbenzene,[16] allylbenzene,[16] *t*-butylbenzene,[16] *sec*-butylbenzene,[16] iso-butylbenzene,[16] and *n*-butylbenzene.[16] In cases for which a methyl group is substitued in the meta position relative to the other alkyl substituent (i.e., 3-*n*-propyltoluene,[11] 3-iso-propyltoluene[16]) the “30 cm^{-1}”

TABLE II. Internal rotational levels and calculated and observed energy spacings in the TOFMS of 4-ethyltoluene.

Level	Energy (cm^{-1})[a]	Transition	Observed E	Calculated E[b]
$0a_1$	0.00	$0a_1 \rightarrow 0a_1$	0.0	0.00
$1e$	5.12	$0a_1 \rightarrow 3a_2$	···	39.53
$2e$	20.30	$0a_1 \rightarrow 3a_1$	55.1	55.03
$3a$	39.53	$1e \rightarrow 1e$	0.0	0.08
$3a$	55.03	$1e \rightarrow 2e$	16.1	15.10
$4e$	84.65	$1e \rightarrow 4e$	78.1	79.45
$5e$	131.00	$1e \rightarrow 5e$	···	125.80

[a] $B = 5.20$ cm^{-1}, $V_6 = 31.00$ cm^{-1}.

[b] Assuming that the spacing between the $0a$ and $1e$ rotational states in S_0 is the same as in S_1 (since the $0a_1 \rightarrow 0a_1$ and $1e \rightarrow 1e$ transitions must be coincident in energy).

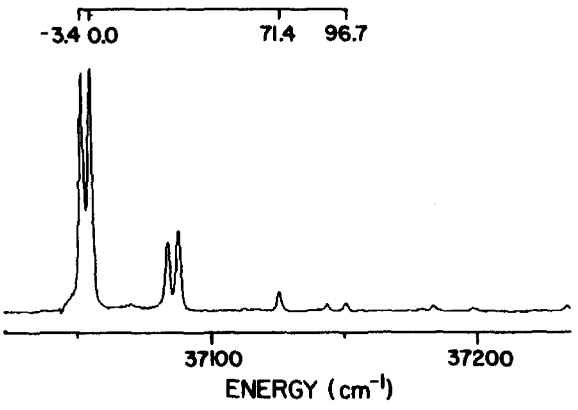


FIG. 7. One-color TOFMS of the 0_0^0 region of the 3-ethyltoluene. The peak at 3.4 cm^{-1} to lower energy of the origin is due to a methyl torsion. Such doublet structure at the origin is indicative of differences in the potential barrier height to methyl rotation in S_1 and S_0. Assignments are given in Table II.

feature occurs as a doublet just as the origin does. Such an occurrence is expected since the $0a_1 \rightarrow 0a_1$ and $1e \rightarrow 1e$ doublet structure at the origin should also be built on all vibronic features.

For 3-ethyltoluene (Fig. 7), the doublet with components at 37 083.0 and 37 087.2 cm^{-1} (29.0 and 33.2 cm^{-1} from the origin, respectively) is due to the $0a_1 \rightarrow 0a_1$ and $1e \rightarrow 1e$ methyl rotor transitions built on the ethyl torsional feature observed for ethylbenzene (Fig. 1) at 28.6 cm^{-1} to higher energy of the origin.

The feature in Fig. 7 at 71.4 cm^{-1} to higher energy of the origin does not appear in Fig. 1 for ethylbenzene and is most likely due to a methyl rotational transition.

Table III lists the calculated fit of the spectrum for a methyl rotor with $B = 5.4$ cm^{-1}, $V_3 = 78$ cm^{-1}, and $V_6 = 0$ cm^{-1}. The zero-point energy for the methyl motion is 26.2 cm^{-1}.

G. 2-Ethyltoluene

The TOFMS of jet-cooled 2-ethyltoluene is presented in Fig. 8. The single intense feature at 37 198.9 cm^{-1} is assigned as the origin. The remaining features at higher energy in the spectrum are a mix of methyl rotor transitions and ethyl torsions. While one cannot with certainty identify these latter features, one possible model is presented in Table IV: most of the observed features are assigned as methyl rotor transitions with $B = 5.5$ cm^{-1}, $V_3 = 89$ cm^{-1}, and a resultant methyl torsion zero point energy of 28.8 cm^{-1}. These values are similar to those obtained for the methyl rotor in 2-*n*-propyltoluene.[11]

TABLE III. Internal rotational levels and calculated and observed energy spacing in the TOFMS of 3-ethyltoluene.

Level	Energy (cm^{-1})[a]	Transition	Observed E	Calculated E[b]
$0a$	0.00	$0a \rightarrow 0a$	0.0	0.00
$1e$	1.61	$0a \rightarrow 3a$	···	58.80
$2e$	42.77	$0a \rightarrow 3a$	71.4	71.50
$3a$	58.80	$1e \rightarrow 1e$	− 3.4	− 3.39
$3a$	71.50	$1e \rightarrow 2e$	···	37.77
$4e$	101.83	$1e \rightarrow 4e$	96.7	91.83
$5e$	149.35	$1e \rightarrow 5e$	···	144.35

[a] $B = 5.40$ cm^{-1}, $V_3 = 78.00$ cm^{-1}.

[b] Assuming a spacing of 5.00 cm^{-1} between the $0a$ and $1e$ rotational states in S_0.

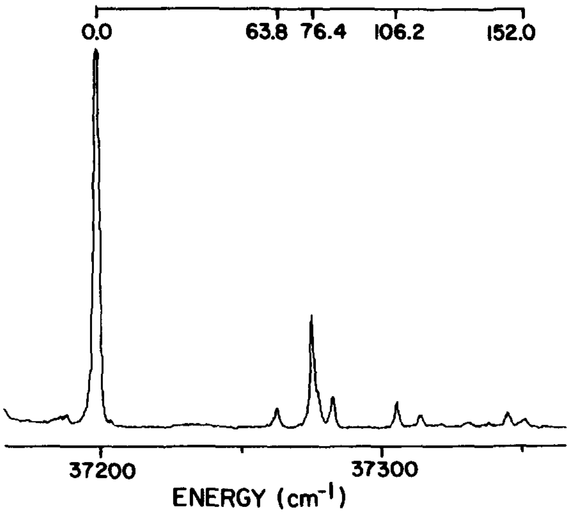


FIG. 8. One-color TOFMS of the 0_0^0 region of 2-ethyltoluene. Both methyl and ethyl group torsions give rise to the weak features to higher energy of the origin. Assignments of the methyl rotor torsions are given in Table III.

IV. DISCUSSION

A. Diethylbenzenes

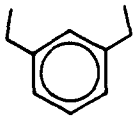
The orientation of the ethyl groups in diethylbenzene can be determined by counting the number of origins present in the TOFMS of 1,3-diethylbenzene. As only a single origin is observed in the TOFMS of ethylbenzene itself, only one of the many possible ethyl rotamers (cf. **3–5**) is a stable conformational minimum. If the most energetically favorable orientation for the ethyl group with respect to the benzene plane is such that all ethylbenzene carbon atoms are coplanar, three distinct conformations of 1,3-diethylbenzene are possible:

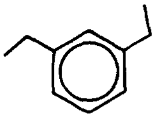
TABLE IV. Internal rotational levels and calculated and observed energy spacings in TOFMS of 2-ethyltoluene.

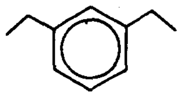
Level	Energy (cm^{-1})[a]	Transition	Observed E	Calculated E[b]
$0a$	0.00	$0a \rightarrow 0a$	0.0	0.00
$1e$	1.36	$0a \rightarrow 3a$	63.8	61.95
$2e$	47.15	$0a \rightarrow 3a$	76.4	77.58
$3a$	61.95	$1e \rightarrow 1e$	0.0	0.00
$3a$	77.58	$1e \rightarrow 2e$	···	45.79
$4e$	107.15	$1e \rightarrow 4e$	106.2	105.79
$5e$	155.26	$1e \rightarrow 5e$	152.0	153.90

[a] $B = 5.50$ cm^{-1}, $V_3 = 89.00$ cm^{-1}.

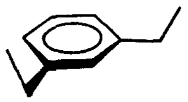
[b] Assuming that the spacing between the $0a$ and $1e$ rotational states in S_0 is the same as in S_1 (since the $0a \rightarrow 0a$ and $1e \rightarrow 1e$ transitions must be coincident in energy).



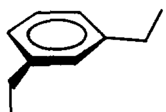




If the terminal carbon atoms of the ethyl groups project up out of the plane of the benzene ring (cf. **4**), only two conformations are possible:



syn



anti

Since the TOFMS for 1,3-diethylbenzene (Fig. 3) shows only two origins, the latter two conformations (*syn* and *anti*) must correspond to energy minima for the molecule. This illustrates the ability of laser jet spectroscopy to observe and identify individual stable conformations of nonrigid aromatic molecules. Although the difference in the energy of the $S_1 \leftarrow S_0$ transition for the *syn* and *anti* conformations is small (9 cm^{-1} for 1,3-diethylbenzene and 4.1 cm^{-1} for 1,4-diethylbenzene), it is more than enough for the two origins to be resolved in the TOFMS.

The relative intensities of the two origins in the TOFMS of 1,2-diethylbenzene leads to the assignment of the lower energy origin as the *syn* conformation. For this reason, the lower energy origins in both the meta and para isomers are also assigned as the *syn* conformations. The lower energy origin in both the 1,3- and 1,4-diethylbenzene spectra are also less intense than the higher energy (*anti*) origin.

The separation between the *syn* and *anti* origins decreases in the order, 1,2-diethylbenzene (16.9 cm^{-1}) > 1,3- (9.0 cm^{-1}) > 1,4- (4.1 cm^{-1}). This trend can be explained by the decrease in steric hindrance experienced by the *syn* conformation relative to the *anti* conformation through the series 1,2-, 1,3-, 1,4-diethylbenzene. The steric hindrance between ethyl groups is large enough in the *syn* conformation of the 1,2-isomer that the molecule exists primarily in the *anti* configuration under the conditions of the supersonic expansion.

For 3-propyltoluene and propylbenzene, the *gauche* conformations are found to be red shifted relative to the corresponding *anti* conformations in their TOFMS.[8,11] This shift to lower energy for the *gauche* conformations is attributed to a "self-solvation" of the aromatic ring by the propyl substituent. The lower energy origin of the *syn* conformation of 1,2-diethylbenzene may again be due to a self-solvation mechanism between the two alkyl substituents, i.e., a stabilizing steric effect.

These experimental results are further confirmed by our MOMM-85 calculations. As shown in Table I, the minimum energy conformations for all the diethylbenzenes are the *syn* and *anti* conformations in which the ethyl group is orthogonal to the plane of the benzene ring (cf. **4**). A similar result is found for ethylbenzene and the ethyltoluenes. Interestingly, a third, less stable conformation (local minimum) is found for the 1,2-diethylbenzene in which one of the two ethyl groups is in the plane of the benzene ring. A portion of the steric energy/potential energy surface for 1,2-diethylbenzene is shown in Fig. 5. The third minimum is essentially a shoulder on the *syn* conformation's energy well. Importantly, the calculated heats of formation closely match the experimentally found values (cf. Table I).

The TOFMS of ethylbenzene (Fig. 1) displays two weak features to higher energy of the origin, at 28.6 and 98.0 cm^{-1}. These features cannot be due to internal rotation of the terminal methyl rotor of the ethyl chain because a sensible fit using a three- or sixfold potential well, as has been done in the past for other molecules,[10,11] cannot be found. For this reason, these features are simply attributed to torsional motion of the ethyl chain. The TOFMS of 1,4-diethylbenzene (Fig. 2) reveals many more features to higher energy of the origin than does the TOFMS of ethylbenzene. Some correspondence does seem to exist, however, since Fig. 2 displays features at 26.8 and 115.6 cm^{-1} from the first origin peak at 37 008.9 cm^{-1}, and a second set at 32.7 and 121.3 cm^{-1} from the other origin, at 37 013.0 cm^{-1}. These features are attributed to torsions of the ethyl groups, as in ethylbenzene. The remaining features in Fig. 2, which have no counterparts in Fig. 1, are either due to coupled motions of the two ethyl groups in diethylbenzene, or to internal rotation of the terminal methyl groups of the ethyl chains. This latter possibility is not likely for several reasons: (1) ethylbenzene does not exhibit such transitions, (2) the potential barrier for the methyl rotation should be threefold (V_3), yet such a potential cannot account for the observed spectrum, and (3) the barrier to methyl rotation in ground state ethane is calculated to be quite large ($\sim$960 cm^{-1}).[17] The weak features observed to higher energy of the origins in the TOFMS of all three isomers of diethylbenzene are therefore regarded as due to various torsions of the ethyl groups, coupled and uncoupled.

B. Ethyltoluenes

Further experimental evidence that an ethyl group substituted on a benzene ring does not have both carbon atoms in the plane of the ring but in fact has one carbon atom projecting up out of the plane and perpendicular to it, can be obtained upon examination of the TOFMS for 3-ethyltoluene. Due to the asymmetry of this molecule, two origins should be observed in the TOFMS were the ethyl group to lie wholly in the plane of the ring. Since only one origin is in fact observed (Fig. 7), the stable configuration must be with the terminal carbon atom of the ethyl group projecting up out of the plane of the ring.

The potential barriers calculated for methyl rotation in S_1 for the various isomers of ethyltoluene are quite similar to those calculated previously for the *n*-propyltoluenes.[11] The overall height of the experimentally observed barrier to methyl rotation decreases in the order ortho > meta > para, which is consistent with the decrease in steric interaction between the ethyl and methyl groups.

As is observed for ethylbenzene and the diethylbenzenes, numerous features occur in the spectra of the ethyltoluenes which are attributed to ethyl torsions. These torsions are also observed to occur in combination with internal rotation of the ring methyl group, as for example, in the TOFMS of 3-ethyltoluene for which the doublet structure occurring at the origin (due to methyl rotation) also is built on the ethyl torsion which occurs at 33.1 cm^{-1} to the blue of the origin. While it is possible that some of the observed features in the TOFMS of the ethyltoluenes may be due to internal rotation of the terminal methyl group of the ethyl chain, such an assignment is not likely to be correct for the same reasons outlined in the discussion concerning the diethylbenzenes.

V. SUMMARY AND CONCLUSIONS

The fact that TOFMS techniques are capable of resolving the origins for individual stable conformations of molecules such as the diethylbenzenes and the ethyltoluenes has resulted in the determination of the most stable conformation(s) of the ethyl groups in these molecules. Counting the number of origins in the TOFMS of 1,3- and 1,4-diethylbenzene or 3-ethyltoluene leads to the conclusion that the plane defined by the two carbon atoms of the ethyl group and the carbon atom of the ring to which the ethyl group is bonded is perpendicular to the plane containing the ring.

For the ethyltoluenes, the assignment of the methyl torsions in the TOFMS using an expanded free-rotor wave function in conjunction with various three- or sixfold potential wells works well in fitting the spectra and characterizing the potential barriers to rotation. The barrier height decreases in the order ortho > meta > para, also found to be the case for the xylenes and *n*-propyltoluenes, and is attributed to the decrease in steric hindrance which occurs in these isomers. The results for the ethyltoluenes are found to be entirely consistent with those for the xylenes and *n*-propyltoluenes.

It is particularly impressive that origins are seen for the two conformations in these compounds, especially for 1,4-diethylbenzene, given the very small interaction between the substituents which distinguishes one conformation from the other. This suggests strongly that the supersonic molecular jet TOFMS technique will be of further utility in conformational analysis and potential energy evaluations.

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