accompany formation of a less ionic bond. These results emphasize the importance of electrostatic effects in these complexes.

Acknowledgment. This work was conducted under the auspices of the United States Department of Energy. S.M.B. gratefully acknowledges the receipt of a Director's postdoctoral fellowship.

Supplementary Material Available: Geometries (as Z matrices) and energies for all compounds studied (13 pages). Ordering information is given on any current masthead.

A Study of Nonrigid Aromatic Molecules. Observation and Spectroscopic Analysis of the Stable Conformations of Various Alkylbenzenes by Supersonic Molecular Jet Laser Spectroscopy†

Jeffrey I. Seeman,*,[1a] Henry V. Secor,[1a] P. J. Breen,[1b,c] V. H. Grassian,[1b] and E. R. Bernstein*,[1b]

Contribution from the Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261, and the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received April 26, 1988*

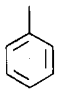
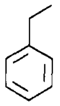
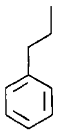
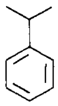
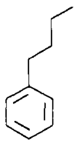
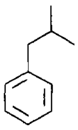
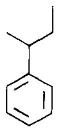
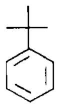
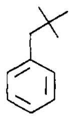
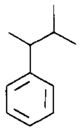
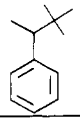
Abstract: The technique of supersonic molecular jet laser spectroscopy was used to determine the stable conformations of a series of alkylbenzenes. This study demonstrates, for the first time, the sensitivity of molecular jet spectroscopy in determining both the number of stable conformations as well as the geometry of various ethyl, propyl, and butyl substituents relative to the aromatic ring. Different rotamers with low barriers to interconversion, <5 kcal/mol, can be isolated in the supersonic jet expansion. Each observed conformation exhibits its own spectroscopic origin ($S_1 \leftarrow S_0$ transition) in a two-color time-of-flight mass spectrum (TOFMS). The number of stable conformations is then used to determine the minimum energy geometries of the substituent group. Previous identification of individual molecular conformations for such low barriers to interconversion has not been attainable with conventional techniques such as variable-temperature NMR.

Molecular conformation and its relationship to the chemical and physical properties of organic molecules have proven to be worthy of the intense effort expended since the pioneering work of D. H. R. Barton in the early 1950's.[2] Nonetheless, the experimental determination of the conformational preferences of many fundamentally important substituents is still lacking.[3] This void is particularly prominent for substituents which have free energy barriers to conformational interconversion of less than ca. 5 kcal mol^{-1} (1750 cm^{-1}), outside the range of variable-temperature NMR spectroscopy. In cases for which the individual conformations have not been "frozen out" and identified using the NMR technique, theoretical calculations have been of considerable value in facilitating conformational analysis and geometry assignments.[4]

Recently, we communicated the results of our initial studies using supersonic molecular jet laser spectroscopy as a novel tool for conformational analysis.[5-8] This technique has allowed us to assign unequivocally the minimum energy geometries of aromatic ethyl and propyl substituents[7,8] and to determine the experimental values for torsional potential barriers in S_0 and S_1 for aromatic methyl groups.[6] The jet spectroscopic technique allows the probing of both ground-state and electronically excited-state features of jet-cooled molecules.

The expansion process results in gas-phase molecules at near absolute zero temperature.[9] Hence, ground-state energy minima can be isolated and studied, even when very low barriers to interconversion are present. Each stable conformation corresponding to a potential energy minimum generates, at least in principle, its own spectroscopic 0_0^0 transition; and conversely, each 0_0^0 transition is associated with a specific stable ground-state conformation. By examining the spectra of specifically substituted alkylbenzenes, one can "count" the number of stable ground-state conformations. Molecular geometry and conformation can be assigned from a knowledge of the number of ground-state energy minima a molecule possesses.

Table I. Substituent Patterns for Substrates Examined in This Work

no. of atoms in substituents	aryl-to-alkyl bond type: primary Ar–CH_2R	secondary Ar–CHR^1R^2	tertiary Ar–$CR^1R^2R^3$
C_1			
C_2			
C_3			
C_4	 		
C_5			
C_6			

[†] Dedicated to Derek Barton, on the occasion of his 70th birthday and to commemorate his seminal research in conformational analysis.

0002-7863/89/1511-3140$01.50/0

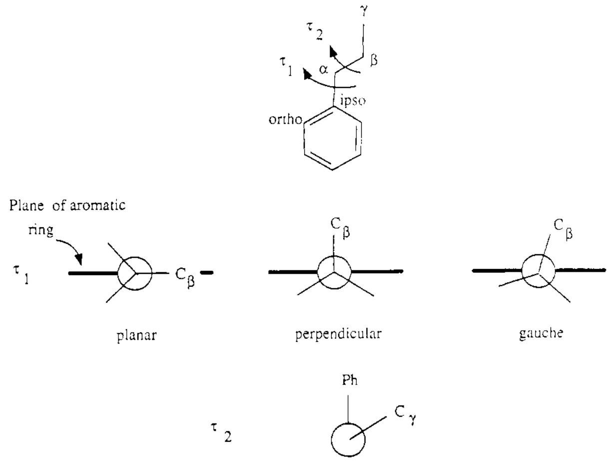


Figure 1. Definition of torsional angles which specify conformational geometries of the molecules examined in this study.

Alkylbenzenes can be divided into three categories with regard to substitution patterns: the aromatic ring can be bonded to a primary, secondary, or tertiary alkyl carbon atom (cf. Table I for the substituents examined herein). In this work, we are primarily interested in two conformational features: first, the orientation of the aromatic ring relative to the alkyl side chain, described by the torsion angle τ_1 (cf. Figure 1) (this is equivalent to defining the position of C_β relative to the plane of the benzene ring); and, second, the orientation of C_γ relative to C_{ipso} (this is described by the torsion angle τ_2). Examination of molecular models and simple symmetry arguments indicate three conformational types for τ_1, as indicated in Figure 1: planar, for which a C_α–C_β bond is in the plane of the aromatic ring; perpendicular, for which a C_α–C_β bond is perpendicular to the plane of the aromatic ring; and gauche, for which $0° < \tau_1(C_{ortho}–C_{ipso}–C_\alpha–C_\beta) < 90°$.

In this report, the two-color time-of-flight mass spectra (TOFMS)[10a] and dispersed emission (DE) spectra of several alkyl-substituted benzenes (cf. Table I) are presented and analyzed in terms of the individual ground-state conformations of these nonrigid molecules.[9,10b] In particular, we consider the following issues. (a) Will supersonic molecular jet spectroscopy allow the observation of different conformations of more complex alkylbenzenes within the propyl and butyl series? (b) Do complex alkyl substituents of the type $ArCH_2R$ (R = alkyl) have $\tau_1 = 90°$ (perpendicular conformation, Figure 1)? (c) Can minimum energy conformations of $ArCHR^1R^2$ and $ArCR^1R^2R^3$ be observed? (d) In addition to observing different conformations, will this technique provide an experimental determination of their geometries?

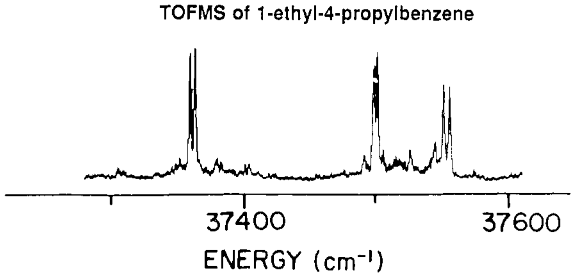
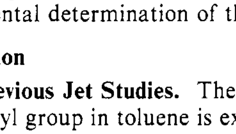


Figure 2. TOFMS of the 0_0^0 region of 1-ethyl-4-propylbenzene (**4**). The spectrum consists of four origins at 37 369.1, 37 372.7 and 37 496.7, 37 497.3 cm^{-1}, corresponding to four stable conformations for this molecule (see text).

Results and Discussion

A. Results of Previous Jet Studies. The barrier to internal rotation of the methyl group in toluene is extremely small due, in part, to the barrier's sixfold symmetry. Hence, assignment of a stable conformational form for this molecule is not meaningful.[6,13,14] Our observation of two 0_0^0 transitions in the TOFMS for both 1,3-diethylbenzene and 1,4-diethylbenzene (corresponding to the syn and anti conformations) and a single 0_0^0 transition for ethylbenzene establishes that the perpendicular conformation **1a** of the aromatic ethyl group in these compounds is present in the global energy minimum.[8]



1a: $R = CH_3$
1b: $R = CH_3CH_2$

---

(1) (a) Philip Morris Research Center. (b) Colorado State University. (c) Current address: Baker Performance Chemicals, 3920 Essex Lane, Houston, TX 77027.

(2) For reviews of this subject and leading references, see: (a) Barton, D. H. R. Some Recollections of Gap Jumping. In *Profiles, Pathways, and Dreams, The Development of Modern Organic Chemistry*; Seeman, J. I., Ed.; American Chemical Society: Washington, D.C., in press. (b) Ramsey, O. B. *Stereochemistry*; Heyden: London, 1981. (c) Eliel, E. L.; Allinger, N. L.; Wilen, S. H. *Topics in Stereochemistry*; Wiley-Interscience: New York; Vol 1–17. (d) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley-Interscience: New York, 1965. (e) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(3) (a) Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: Deerfield Beach, FL, 1985. (b) Jackman, L. M.; Cotton, F. A., Eds. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1975. (c) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* **1985**, *18*, 80. (d) Berg, U.; Sandström, J. *Adv. Phys. Org. Chem.*, in press.

(4) (a) Ōsawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982. (c) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985. (d) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (e) Pross, A.; Radom, L. *Adv. Phys. Org. Chem.* **1981**, *13*, 1. (f) Grunewald, G. L.; Creese, M. W.; Weintraub, H. J. R. *J. Comput. Chem.* **1988**, *9*, 315.

(5) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3453.

(6) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.

(7) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1927.

(8) Breen, P. J.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 3269.

(9) Bernstein, E. R.; Law, K.; Schauer, M. *J. Chem. Phys.* **1984**, *80*, 207.

(10) (a) The name "one- (and two-) color time-of-flight mass spectroscopy" is generally employed to describe the following experiment. A sample is irradiated with a laser of energy ν_1, resulting in the generation of the first excited singlet state ($S_0 \rightarrow S_1$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($S_1 \rightarrow I^+$). The ions are detected in given mass channels by time-of-flight mass spectroscopy, such that only ion current representing a chosen m/z is recorded. The energy of the ν_1 laser is changed, and an absorption spectrum of a mass-selected species is obtained. This technique may also be called mass resolved excitation spectroscopy. (b) In pioneering work, Smalley and co-workers have reported[11a,b] the fluorescence excitation (FE) spectra and dispersed fluorescence spectra of a set of alkylbenzenes. These studies did not examine in detail the conformational analysis of the compounds. In addition, because the FE results are not mass selected, there could be some ambiguity regarding the source of some of the transitions. Ito et al.[11c] have examined intramolecular electronic energy transfer of bichromophoric molecules [e.g., 1-(*o*-tolyl)-3-(*p*-tolyl)propane] using these techniques. Ito's Tohoku University group has also studied conformational problems in phenols and naphthols[11d] and anisoles.[11e] One of us (E.R.B.) has previously examined the TOFMS of propylbenzene clusters with methane, ethane, and propane.[12]

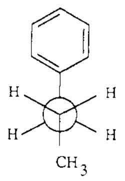
(11) (a) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5039. (b) Hopkins, J. B.; Powers, D. E.; Mukamel, S.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5049. (c) Ebata, T.; Suzuki, Y.; Mikama, N.; Miyashi, T.; Ito, M. *Chem. Phys. Lett.* **1984**, *110*, 597. (d) Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1984**, *88*, 5180. (e) Yamamoto, S.; Okuyama, K.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1986**, *125*, 1.

(12) Law, K. S.; Bernstein, E. R. *J. Chem. Phys.* **1985**, *82*, 2856.

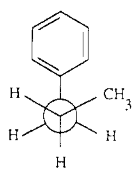
(13) Kreiner, W. A.; Rudolph, H. D.; Tan, B. T. *J. Mol. Spectrosc.* **1973**, *48*, 86.

(14) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817.

For propylbenzene, supersonic molecular jet spectroscopy has shown that the propyl moiety exists in two stable, observable conformations with respect to the aromatic ring: an anti **2** and a gauche **3** conformation.[7] Importantly, these results are consistent only with a perpendicular orientation of the first torsion for both of these conformations, i.e., $\tau_1(\mathrm{C_{ortho}}-\mathrm{C_{ipso}}-\mathrm{C}_\alpha-\mathrm{C}_\beta) = 90°$ as illustrated by **1b** for both **2** and **3**. [Beneath the structures **2** and **3** are the relative values of the MOMM-calculated[14] steric energies (SE) for these rotamers. The SE values are indicative of the relative stabilities of these conformations. Relative SEs are shown below the structures for some of the other conformations discussed in this paper.]



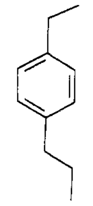
2
0^a



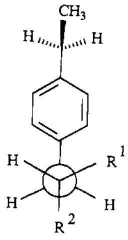
3
0.39^a

^{a}Steric energy (kcal/mol) (rel).

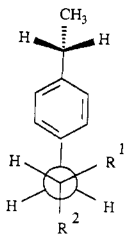
B. Compounds Containing an Aryl to a Primary Alkyl Bond (ArCH$_2$R). To probe the extent of the applicability of this supersonic jet technique for the structure determination of more complex molecules, we first studied a series of compounds containing the Ar–CH$_2$R substructure. 1-Ethyl-4-propylbenzene (**4**) is an interesting combination of a molecule containing both the ethyl and propyl substituent. Extrapolating from the results obtained for the ethylbenzenes and propylbenzenes cited above, 1-ethyl-4-propylbenzene would have, in principle, four origins: a syn–anti **5a**, a syn–gauche **5b**, and the corresponding anti–anti **6a** and anti–gauche **6b** (the first descriptor specifying the relative disposition of the two substituents with respect to each other, the second descriptor specifying the conformation of the propyl substituent relative to the aromatic ring). As shown in Figure 2, four origin transitions are observed in the TOFMS of **4**, one each for the four energy minima (at 37 369.1, 37 372.7 and 37 496.7, 37 497.3 cm^{-1}). Given the above structural logic and the TOFMS of the ethyl- and propylbenzenes, the third doublet at ca. 37 548 cm^{-1} then must be assigned as a torsional motion of the propyl substituent group in accord with previous work.[5-8]



4

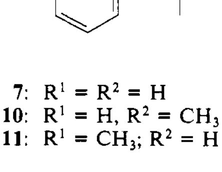


5

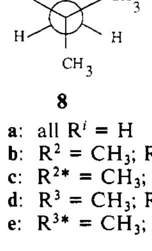


6

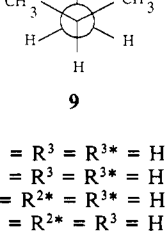
a: R^1 = H; R^2 = CH$_3$
b: R^1 = CH$_3$; R^2 = H



7: R^1 = R^2 = H
10: R^1 = H, R^2 = CH$_3$
11: R^1 = CH$_3$; R^2 = H



8



9

a: all R^i = H
b: R^2 = CH$_3$; R^{2*} = R^3 = R^{3*} = H
c: R^{2*} = CH$_3$; R^2 = R^3 = R^{3*} = H
d: R^3 = CH$_3$; R^2 = R^{2*} = R^{3*} = H
e: R^{3*} = CH$_3$; R^2 = R^{2*} = R^3 = H

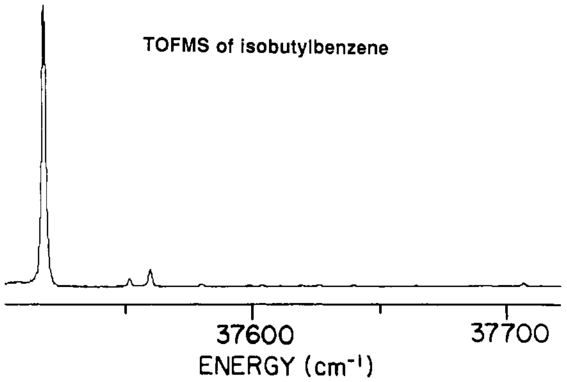


Figure 3. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of isobutylbenzene (**7**). The spectrum displays a single origin at 37 517.8 cm^{-1}. The weak features at 37 551.4 and 37 559.6 cm^{-1} are attributed to torsional motion of the isobutyl group.

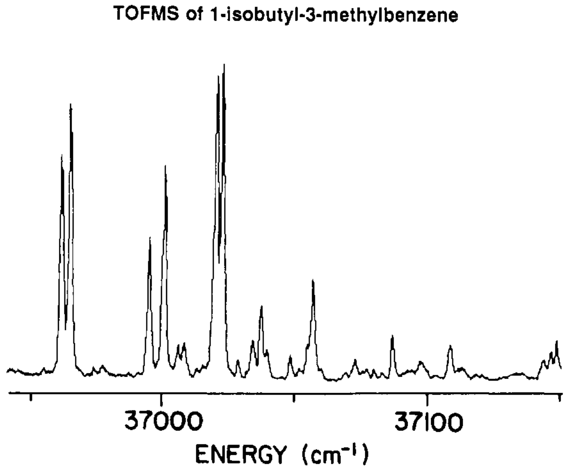


Figure 4. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-isobutyl-3-methylbenzene (**10**). The spectrum contains two origins at 36 965.1 and 37 023.0 cm^{-1}. The peaks occurring 3 cm^{-1} lower in energy than these origins are due to ring methyl torsions.

The TOFMS for the 0_0^0 region of the $S_1 \leftarrow S_0$ transition in isobutylbenzene (**7**) is presented in Figure 3. The spectrum displays a single intense origin at 37 517.8 cm^{-1}. Two weak features, assigned as isobutyl torsions, occur at 37 551.4 and 37 559.6 cm^{-1}. Comparison of this spectrum to that of propylbenzene[7,12] is of value since the TOFMS of propylbenzene clearly displays two origins, corresponding to conformations **2** (anti) and **3** (gauche). Addition of a methyl group to the β position of the propyl chain results in an isobutyl group. The two possible conformations for isobutylbenzene, analogous to **2** and **3**, are **8a** and **9a**.

Which of the two conformations **8a** or **9a** corresponds to the minimum energy conformation of isobutylbenzene can be determined experimentally from examination of the TOFMS of 1-isobutyl-3-methylbenzene (**10**). Because of the asymmetrically substituted aromatic ring, the TOFMS for **10** would contain two origins if **8d** and **8e** were the minimum energy conformations; conformation **9d** (=**9e**) would show only a single origin. The spectrum displayed in Figure 4 evidences two origins, at 36 965.1 and 37 023.0 cm^{-1} (with 1e $\leftarrow$ 1e ring methyl torsions occurring $\sim$3 cm^{-1} to lower energy of each origin[6,7]) so that **8d** and **8e** must be the minimum energy conformers. This conclusion is supported by our MOMM calculations, in which **8a** is found to be more stable than **9a** by ca. 0.7 kcal mol^{-1} as judged by steric energies. Statistical weights also favor **8a** over **9a**. These results reflect the greater stability of anti conformations relative to gauche conformations in isobutylbenzenes, a relationship also observed and calculated for the cases of propylbenzene and related molecules. Just as in the cases of propylbenzene and 3-methyl-1-propylbenzene, the number of conformations observed for isobutylbenzene and 3-methylisobutylbenzene also dictate that $\tau_1(\mathrm{C_{ortho}}-\mathrm{C_{ipso}}-\mathrm{C}_\alpha-\mathrm{C}_\beta) = 90°$ for the isobutyl substituent.[3c,d,15]

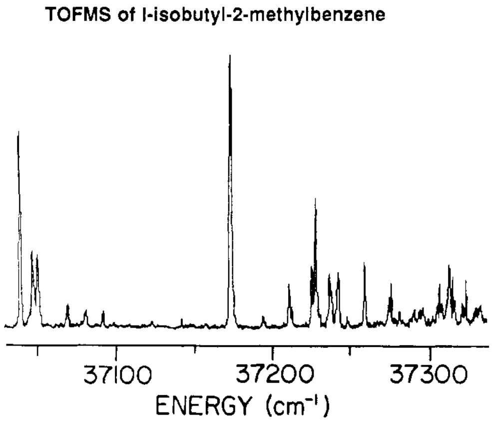


Figure 5. TOFMS of the 0_0^0 region of 1-isobutyl-2-methylbenzene (**11**). Two origins are observed in the spectrum at 37 036.0 and 37 171.8 cm^{-1}.

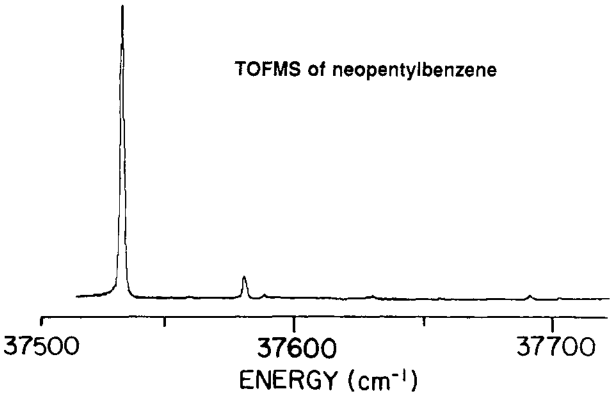
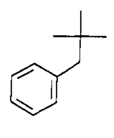


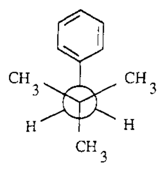
Figure 6. TOFMS of the 0_0^0 region of neopentylbenzene (**12**). The spectrum shows only one origin at 37 533.6 cm^{-1}. Weaker features, higher in energy than the origin, are attributed to low-frequency torsional motions of the neopentyl group.

The TOFMS of 1-isobutyl-2-methylbenzene (**11**) (Figure 5) contains two origins at 37 036.0 and 37 171.8 cm^{-1}. These presumably correspond to **8b** and **8c**. As conformation **9** is not a significantly populated energy minimum for either isobutylbenzene or 1-isobutyl-3-methylbenzene, the observation of two origins for 1-isobutyl-2-methylbenzene is further support for conformations **8b** and **8c** for these isobutylbenzenes.

The TOFMS of neopentylbenzene (**12**) is shown in Figure 6.



12



12a

A single origin is observed at 37 533.6 cm^{-1}. The observation of a single origin is consistent with the findings for propylbenzene and the isobutylbenzenes discussed above. As in the case for other compounds containing an aryl to a primary alkyl bond, τ_1-(C_{ortho}–C_{ipso}–C_α–C_β) = 90° for neopentylbenzene.[15] As illustrated in **12a**, only a single staggered conformation is possible about τ_2. These results are confirmed by MOMM calculations which indicate that the minimum energy conformation of **12** has a staggered arrangement about the C_α–C_β bond (τ_2) and has τ_1-(C_{ortho}–C_{ipso}–C_α–C_β) = ca. 90°.

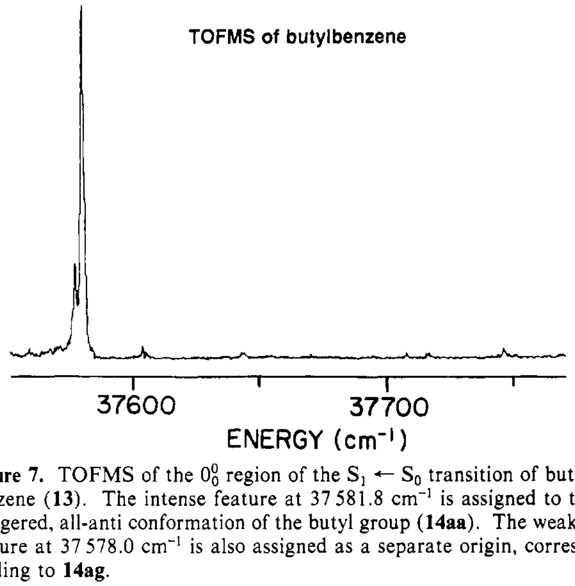
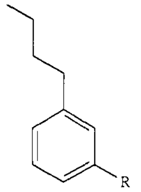


Figure 7. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of butylbenzene (**13**). The intense feature at 37 581.8 cm^{-1} is assigned to the staggered, all-anti conformation of the butyl group (**14aa**). The weaker feature at 37 578.0 cm^{-1} is also assigned as a separate origin, correspoinding to **14ag**.

The TOFMS for the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of butylbenzene (**13**) is presented in Figure 7. The spectrum contains one intense origin, at 37 581.8 cm^{-1}, with what appears to be a weaker origin to lower energy, at 37 578.0 cm^{-1}. This latter peak is unlikely to be due to a methyl rotor transition for a methyl group so far removed from the chromophore.[5-8] A variety of conformations, built on the anti and gauche conformations of propylbenzene, can be imagined for butylbenzene. If the intense origin feature at 37 581.8 cm^{-1} is indeed due to a single molecular conformation, it is most likely associated with the extended conformation **14aa** (Table II), involving the staggered, all-anti form of the butyl group. This conformer involves the least amount of steric interference, according to our MOMM calculations.[8,14] The assignment is consistent with our previous observations that the anti conformer is energetically favored over the gauche. The less intense origin at 37 578.0 cm^{-1} is only 3.8 cm^{-1} lower in energy than the origin for **14aa**. In propylbenzene, the gauche and anti conformer origins are separated by 49.2 cm^{-1}.[5,7] This range of separation would also be expected between origins belonging to conformations of butylbenzene based on the gauche and anti conformations of propylbenzene. The observed separation of 3.8 cm^{-1} in Figure 6 implies that the second origin (at 37 578.0 cm^{-1}) is probably due to a conformation such as **14ag**. The terminal methyl group of the butyl chain is far enough from the π-system of the ring so that the effect of its orientation on the energy of the π–π^* transition should be relatively small, which is an expectation consistent with the observed spacing of 3.8 cm^{-1}.



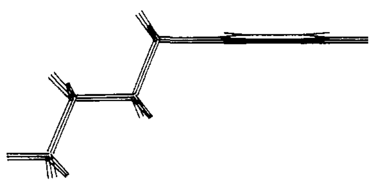
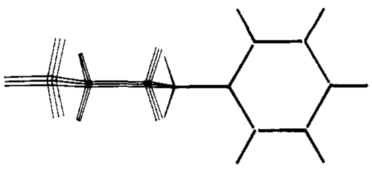
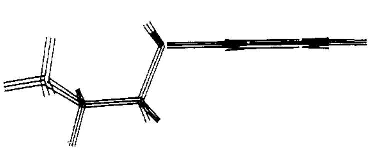
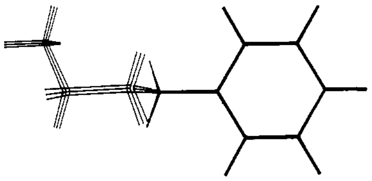
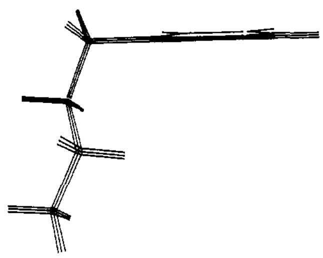
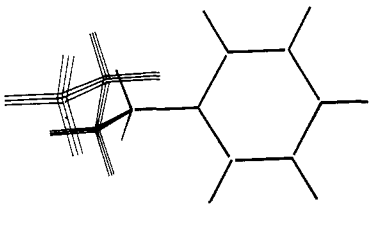
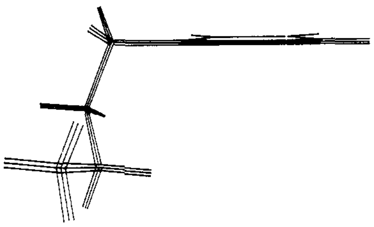
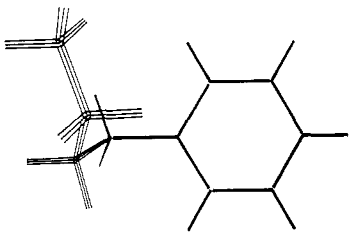
13: R = H
15: R = CH$_3$

We cannot at present account for the failure to observe additional 0_0^0 transitions corresponding to the two other conformations of butylbenzene (gauche/gauche **14gg** and gauche/anti **14ga**) expected based on simple conformational analysis concepts or on our MOMM calculations (Table II). Conformational preferences for various alkylbenzenes, including butylbenzene, have recently been examined using CAMSEQ, MM2, and molecular dynamics methods, with particular attention being placed on "folded" conformations.[4f] The theoretical approaches do not always lead to the same stability ordering of the various possible conformations,[4f] and more detailed experimental studies are indicated.

---

(15) (a) Pettersson, I.; Rang, K.; Sandström, J. *Acta Chem. Scand.* **1986**, *B40*, 751. (b) Roussel, C.; Gallo, R.; Metzger, J.; Sandström, J. *Org. Magn. Reson.* **1980**, *14*, 120. (c) Roussel, C.; Blaive, B.; Gallo, R.; Metzger, J.; Sandström, J. *Org. Magn. Reson.* **1980**, *14*, 166.

Table II. MOMM-85 Calculated Steric Energies for Minimum Energy Conformations of Butylbenzene

conformation	SE (kcal/mol) (rel)		
14aa	0		
14ag	1.85		
14ga	1.30		
14gg	2.02		

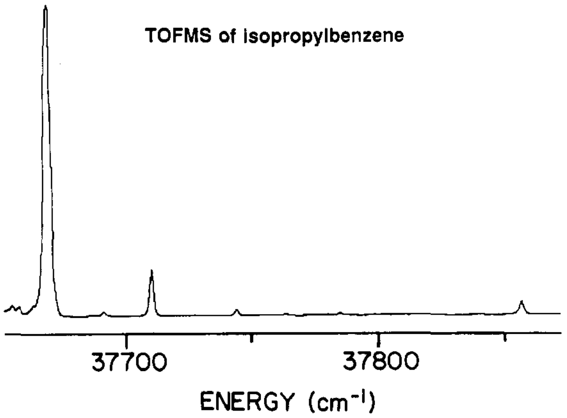
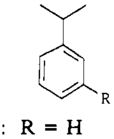


Figure 8. TOFMS of the 0_0^0 region for the $S_1 \leftarrow S_0$ transition of isopropylbenzene (**16**). The sole origin occurs at 37 668.5 cm^{-1}. The weaker feature at 37 710.0 cm^{-1} is attributed to torsional motion of the isopropyl group.

Previous papers from our laboratory have addressed the possibility that local, but not global, stable molecular conformations in nonrigid molecules or in van der Waals clusters can be depopulated through collisions in the molecular jet expansion.[7] In molecules or clusters for which shallow wells and small barriers to conformational changes exist, energetic collisions may depopulate local minima in the potential surface in favor of the deeper, global ones. Thus, in certain "sterically hindered" compounds (e.g., 2-propyltoluene,[7] 1,2-diethylbenzene,[8] and 1,2-dimethoxybenzene[16b]), not all of the conceivable locally stable orientations of the nonrigid moiety are equally populated. This unequal distribution of conformers in the final expansion equilibrium results in either unequal conformer spectroscopic intensities, or in extreme cases, the failure to observe specific 0_0^0 transitions. Further evidence to substantiate the existence of this "kinetic effect" is presented below.

1-Butyl-3-methylbenzene (**15**) was examined with the hope that asymmetric substitution would confirm the anti/anti conformational assignment of the parent butylbenzene spectrum. Unfortunately, no ion signals could be observed. We attribute this finding to enhanced modes of nonradiative decay from S_1 of **15**, thereby rendering the TOFMS experiment untenable in this case.

C. Compounds Containing an Aryl to a Secondary Alkyl Bond ($ArCHR^1R^2$). Isopropylbenzene (**16**) is the prototype of molecules



16: R = H
20: R = CH_3
21: R = CH_3CH_2

containing an aryl–secondary alkyl bond. Because the internal rotation barrier about the C_{sp^2}–C_{sp^3} bond of isopropylbenzene is less than 5 kcal mol^{-1},[17] NMR studies have been unable to isolate

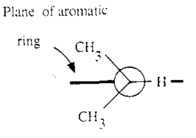
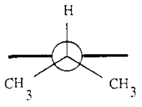
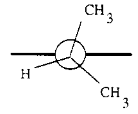
---

(16) (a) Seeman, J. I.; Secor, H. V.; Breen, P. J.; Bernstein, E. R. *J. Chem. Soc., Chem. Commun.* **1988**, 393. (b) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.*, in press.

(17) The rotational barrier about the $C_{sp}{}^2$–$C_{sp}{}^3$ for isopropylbenzene has been reported to be 0.25 kcal mol^{-1} by low-resolution microwave investigations[18a] and 2.0 kcal mol^{-1} by NMR studies.[18b] Recent MOMM calculations have estimated a barrier of 2.3 kcal mol^{-1}.[14]

(18) (a) True, N. S.; Farag, M. S.; Bohn, R. K.; MacGregor, M. A.; Radhakrishnan, J. *J. Phys. Chem.* **1983**, *87*, 4622. (b) Schaefer, T.; Parr, W. J. E.; Danchura, W. *J. Magn. Reson.* **1977**, *25*, 167.

Table III. Number of Conformations of Various Isopropylbenzenes Based on Experiment and Conformational Analysis Predictions

	no. of conformations			
	predicted[a]			
	Plane of aromatic ring 			
compd	**17** planar[b]	**18** perpendicular[b]	**19** gauche[b]	obsd[c]
isopropylbenzene (**16**)	1	1	1	1
1-isopropyl-3-methylbenzene (**20**)	2	1	2	2
1-ethyl-3-isopropylbenzene (**21**)	2	2	4	2

[a] Based on counting all possible molecular conformations having the specific substituent conformation depicted, but counting degenerate conformations only once. [b] This term refers to the relative position of the α-H and the plane of the aromatic ring. [c] Number of origin transitions observed by TOFMS. See text for additional discussion.

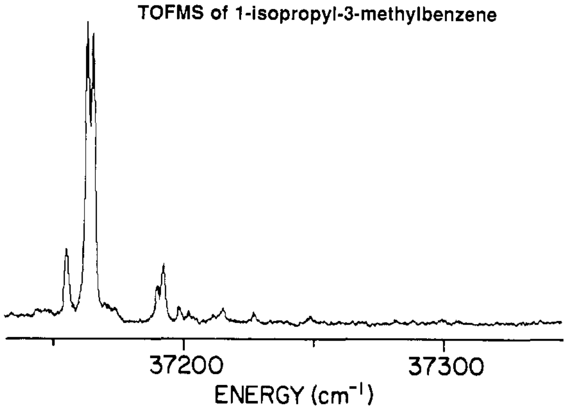


Figure 9. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-isopropyl-3-methylbenzene (**20**). The peak at 37 165.9 cm^{-1} is an origin which forms a doublet with the peak at 37 164.0 cm^{-1}. This latter peak is attributed to the $1e \leftarrow 1e$ internal rotational transition of the ring methyl rotor. The weaker peak at 37 156.0 cm^{-1} is also assigned as an origin. The presence of two origins eliminates **18** as a possible stable conformation.

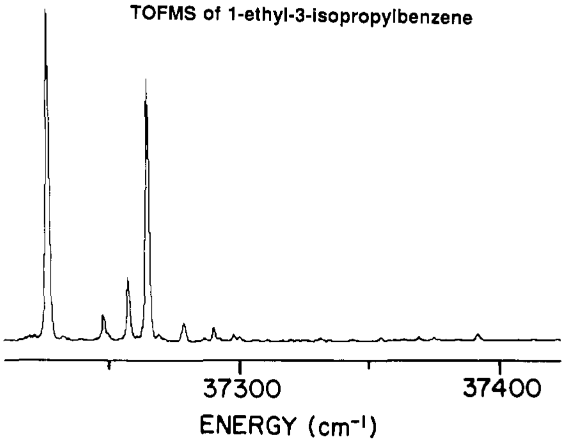


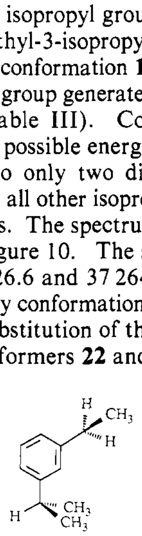
Figure 10. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-ethyl-3-isopropylbenzene (**21**). The two origins of the spectrum, at 37 226.6 and 37 264.8 cm^{-1}, help identify the stable conformation of the isopropyl group as **17**, as outlined in the text.

and identify specific isopropyl conformations for sterically unhindered molecules.[3]

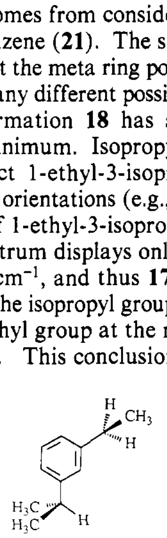
Figure 8 contains the TOFMS of the 0_0^0 region for the $S_1 \leftarrow S_0$ transition of isopropylbenzene. The spectrum consists of a single intense origin at 37 668.5 cm^{-1} and a much weaker feature at 37 710.0 cm^{-1}, the latter attributed to torsional motion of the isopropyl group.[5-8] Table III illustrates the three possible conformations **17**–**19** of isopropylbenzene (**16**). The presence of a single origin indicates that only one conformation of isopropylbenzene is an energy minimum. Determination of which this is may, in principle, be made based on the number of 0_0^0 transitions in the TOFMS of appropriately substituted isopropylbenzene derivatives. The simplest derivatives are 1-isopropyl-3-methylbenzene (**20**, Table III) and 1-ethyl-3-isopropylbenzene (**21**, Table III).

The TOFMS for 1-isopropyl-3-methylbenzene (**20**), presented in Figure 9, contains two origins: the doublet at ca. 37 165 cm^{-1} and a less intense feature at 37 156.0 cm^{-1}. Meta-substituted toluenes have been observed in the past[7-9] to display a doublet feature with a spacing of 2–4 cm^{-1} for the 0_0^0 transition shown to be due to methyl rotor transitions. The feature at 37 156.0 cm^{-1} is neither a hot band nor a methyl rotor internal transition; its relative intensity is independent of cooling conditions and its energy is too low for the appropriate methyl rotor energetics. The weak doublet feature centered at 37 191.8 cm^{-1} is taken to be due to torsional motion of the isopropyl group, as is suggested for isopropylbenzene, but also with the $1e \leftarrow 1e$ ring methyl rotational transition built on it. The presence of two origins in the TOFMS of 1-isopropyl-3-methylbenzene eliminates **18** (which should generate only one origin) as an energy minimum of the isopropyl substituent but does not distinguish between **17** and **19** (Table III).

Experimental determination of the minimum energy orientation of the aromatic isopropyl group comes from consideration of the TOFMS of 1-ethyl-3-isopropylbenzene (**21**). The substitution of an ethyl group (conformation **1a**) at the meta ring position relative to the isopropyl group generates many different possible molecular conformers (Table III). Conformation **18** has already been eliminated as a possible energy minimum. Isopropyl orientation **17** gives rise to only two distinct 1-ethyl-3-isopropylbenzene conformers, but all other isopropyl orientations (e.g., **19**) generate four conformers. The spectrum of 1-ethyl-3-isopropylbenzene is presented in Figure 10. The spectrum displays only two intense origins at 37 226.6 and 37 264.8 cm^{-1}, and thus **17** must be the minimum energy conformation of the isopropyl group with respect to the ring. Substitution of the ethyl group at the meta position then yields conformers **22** and **23**. This conclusion agrees with our MOMM calculations and with the other literature data[3c,d] which likewise predict **17** to be the stable conformation for isopropylbenzene. [**Note Added in Proof**: The TOFMS of 1-fluoro-3-isopropylbenzene shows two features in the 0_0^0 transition region which is consistent with the planar conformation **17** being the minimum energy form of the isopropyl group. H.-S. Im, E.



22



23

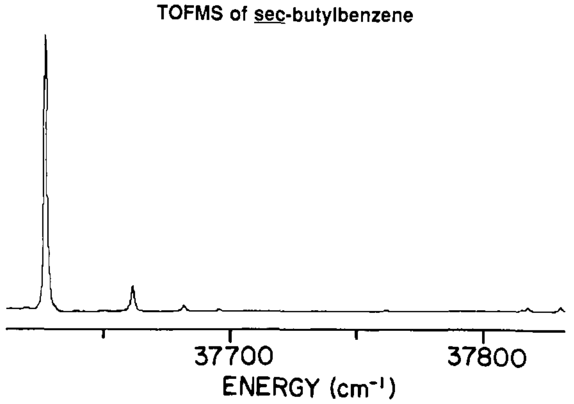
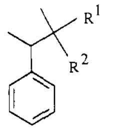


Figure 11. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of *sec*-butylbenzene (**24**). The spectrum displays a single origin at 37 627.1 cm^{-1}. The weak feature at 37 661.3 cm^{-1} is attributed to torsional motion of the *sec*-butyl group.

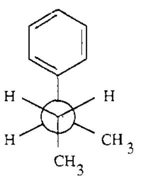
R. Bernstein, H. V. Secor, and J. I. Seeman, unpublished results.]

We next examine the series of three compounds **24**–**26** which is interesting because it embodies the partial substructures of both the isopropyl and propyl substituents.

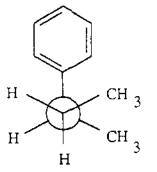


24: R^1 = R^2 = H
25: R^1 = CH$_3$; R^2 = H
26: R^1 = R^2 = CH$_3$

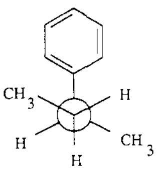
The TOFMS of *sec*-butylbenzene (**24**) in the 0_0^0 region of the $S_1 \leftarrow S_0$ transition is presented in Figure 11 and contains a single origin at 37 627.1 cm^{-1}. The weaker feature occurring at 37 661.3 cm^{-1} is presumably due to torsional motion of the alkyl group as discussed earlier. Only a single conformation for *sec*-butylbenzene is observed. As a first approximation, $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-H_\alpha)$ should equal 0° for *sec*-butylbenzene (**24**) as found for isopropylbenzene.[15a] The Newman projections of the three staggered conformations are illustrated by **27**–**29**. The most stable conformation of *sec*-butylbenzene is **29** by MOMM calculations, nearly 1 kcal mol^{-1} more stable than **27** and 3 kcal mol^{-1} more stable than **28**. We therefore suggest that the minimum energy conformation of *sec*-butylbenzene observed in the jet corresponds to **29**.



27
0.81^a



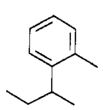
28
2.94^a



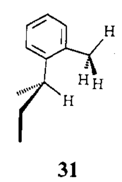
29
0^a

^{a}Steric Energy (kcal/mol) (rel)

The TOFMS of 1-*sec*-butyl-2-methylbenzene (**30**) contains only a single origin (Figure 12). MOMM calculations support the observation of only a single conformation and that the preferred conformation is **31**.



30



31

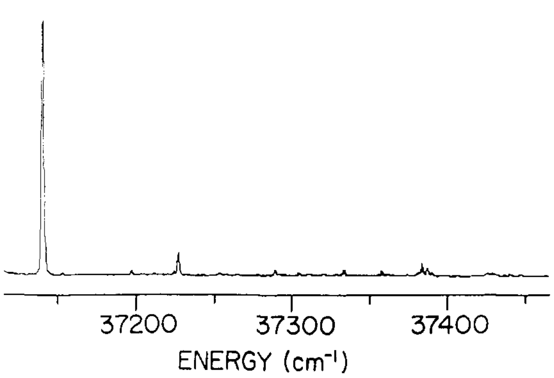
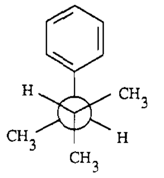
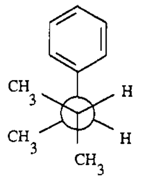


Figure 12. TOFMS of the 0_0^0 region of 1-*sec*-butyl-2-methylbenzene (**30**). The spectrum contains only a single origin. This is consistent with MOMM calculation which predicts only one stable conformation for this molecule (see text).

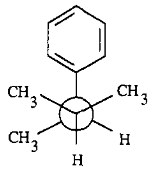
(1,2-Dimethylpropyl)benzene (**25**) can, in principle, exist in one or more of three staggered conformations **32**–**34**. MOMM calculations indicate that conformation **32**, possessing only two gauche–gauche interactions, is the ground-state energy minimum. The TOFMS of **25** indicates two origins at 37 556.6 cm^{-1} and 37 585.9 cm^{-1}. The origin to the red (low energy) is approximately 10% the intensity of the second origin. We tentatively assign the 37 556.6-cm^{-1} origin as **33** and the 37 585.9-cm^{-1} origin as **32** based on the relative intensities of the two origins and the calculated relative stabilities.



32
0^a



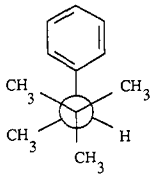
33
0.95^a



34
1.3^a

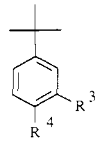
^{a}Steric energy (kcal/mol) (rel).

(1,2,2-Trimethylpropyl)benzene (**26**) has only one staggered conformation, namely, **35**, and its TOFMS shows a single origin at 37 585.8 cm^{-1}.

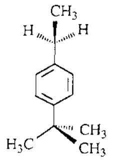


35

D. Compounds Containing an Aryl to a Tertiary Alkyl Bond (ArCR^{1}R^{2}R^3). The one-color TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition for jet cooled *tert*-butylbenzene (**36**) is presented in Figure 13. The spectrum displays a single intense origin at 37 696.2 cm^{-1}, which means that only one of the three postulated conformations (planar **37**, perpendicular **38**, gauche **39**; cf. Table IV) is an energy minimum, and therefore only one of these species

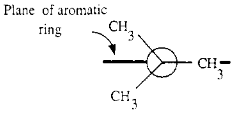
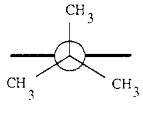
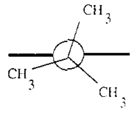


36: R^3 = R^4 = H
40: R^3 = H; R^4 = CH$_3$CH$_2$
42: R^3 = CH$_3$; R^4 = H
45: R^3 = (CH$_3$)$_3$C; R^4 = H



41

Table IV. Number of Conformations of Various *tert*-Butylbenzenes Based on Experiment and Conformational Analysis Predictions

	no. of conformations			
	predicted[a]			
				
compd	**37** planar	**38** perpendicular	**39** gauche	obsd[b]
tert-butylbenzene (**36**)	1	1	1	1
1-*tert*-butyl-4-ethylbenzene (**40**)	1	2	2	1
1-*tert*-butyl-3-methylbenzene (**42**)	2	1	2	2
1,3-di-*tert*-butylbenzene (**45**)	3	2	6	3

[a] Based on counting all possible molecular conformations having the specific substituent conformation depicted, but counting degenerate conformations only once. [b] Number of origin transitions observed by TOFMS. See text for additional discussion.

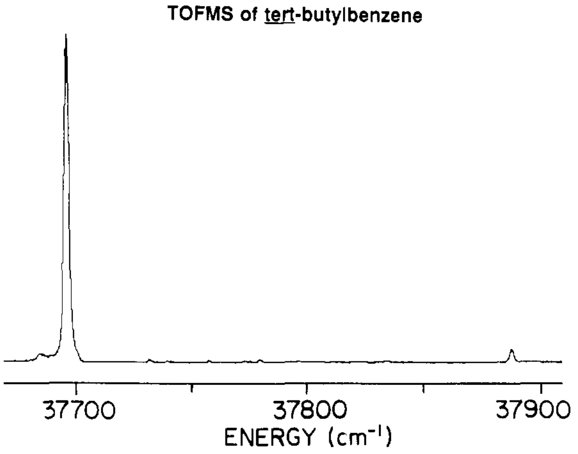
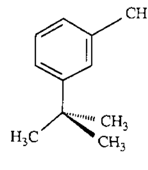


Figure 13. The one-color TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of *tert*-butylbenzene (**36**). The single origin in the spectrum occurs at 37 696.2 cm^{-1} and is indicative of a single stable molecular conformation.

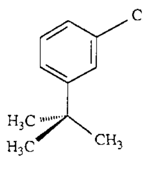
is present in the molecular jet. This is an important conclusion because it implies that the only way that one origin can appear in the TOFMS of 1-*tert*-butyl-4-ethylbenzene (**40**) is if the minimum energy conformation of the *tert*-butyl group corresponds to the planar conformation giving rise to conformation **41**.

The TOFMS for **40**, presented in Figure 14, in fact, contains only one origin at 37 142.0 cm^{-1}. We therefore conclude that the stable conformation for 1-*tert*-butyl-4-ethylbenzene must correspond to **41**. This in turn confirms that the minimum energy conformation of the *tert*-butyl group in *tert*-butylbenzenes must be the planar form and reconfirms the perpendicular conformation of the aromatic ethyl substituent; these structural conclusions follow *if and only if* the conformational assignments for both the *tert*-butyl and ethyl substituents are correct. These conclusions are further supported by our MOMM calculations which predict the planar conformation to be the minimum energy conformation of the *tert*-butyl group in **36** and **40**. Given that both the calculations and the experimental values are in agreement as to the number and position of potential minima on those two surfaces, we conclude that these determinations are valid.

According to the above results, 1-*tert*-butyl-3-methylbenzene (**42**) should exhibit a TOFMS containing two origins, corresponding to conformations **43** and **44**. The TOFMS for the 0_0^0 region of the $S_1 \leftarrow S_0$ transition for **42** using 140 psig of helium



43



44

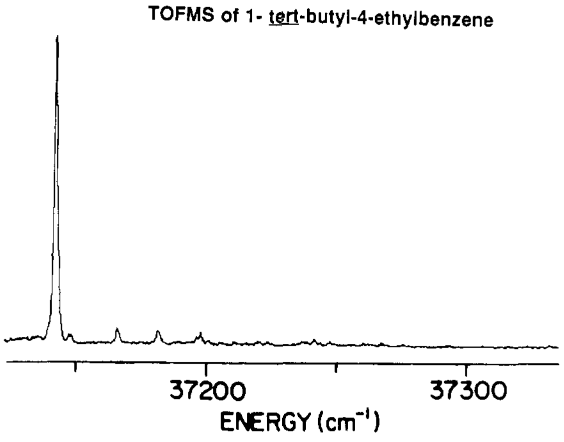


Figure 14. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-*tert*-butyl-4-ethylbenzene (**40**). The fact that this spectrum contains only one origin at 37 142 cm^{-1} identifies the stable molecular conformation of the *tert*-butyl group as **31**.

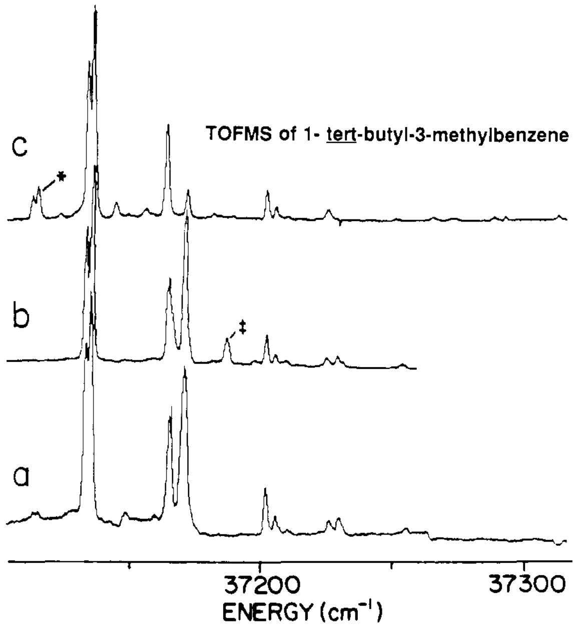


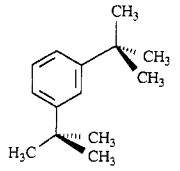
Figure 15. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-*tert*-butyl-3-methylbenzene (**42**), using (a) 140 psig of helium; (b) 1% CF_4 in 100 psig of helium; and (c) 20 psig of argon as the carrier gas. The peaks indicated by the * and ‡ are due to argon and CF_4 clusters, respectively, decomposing into the 1-*tert*-butyl-3-methylbenzene mass channel. The intense peaks at 37 137.0 and 37 169.8 cm^{-1} are origins for two different molecular conformations. The 37 169.8-cm^{-1} peak disappears in (c) because of a kinetic effect discussed in the text.

is presented in Figure 15a. The most intense feature of the spectrum occurs as a barely resolved doublet (due to the methyl rotor transitions[6-8]) centered at 37 136 cm^{-1}. Figure 15a also displays two other intense features at 37 165.0 and 37 169.8 cm^{-1}. Some of the weaker features that appear in the TOFMS of **42** correspond to additional internal rotational transitions of the ring methyl rotor. The spectrum presented in Figure 15a is more complicated than anticipated because there are three relatively intense peaks.

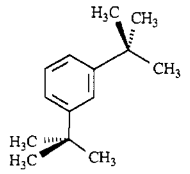
Because the three main features in the TOFMS of **42** are quite intense, the exact assignment of origins and thus the number of conformations for this molecule is not readily apparent. In order to resolve this conformational analysis question, three additional approaches were pursued: temperature-dependent spectra, to investigate the possibility of hot bands (Figure 15); dispersed emission studies (Figure 16); and methyl rotor calculations. The latter demonstrate that the three features cannot be assigned to a single conformation with (even intense) methyl rotor transitions. On a first level of interpretation, Figures 15 and 16 suggest somewhat contradictory conclusions about these data. The peak at 37 169.8 cm^{-1} in Figure 15 appears to be a hot band as its intensity decreases with high-pressure argon expansion. Conclusively, the DE spectrum associated with the 37 169.8-cm^{-1} feature, a portion of which is depicted in Figure 16, indicates that this feature is not a hot band because there are no transitions to higher energy of the excitation energy.

These three results (TOFMS, DE, and rigid rotor calculations) can be rationalized by assigning the feature in question as due to a second conformation of **42** which can be depopulated in the argon expansion. The conformational energy balance (well depth, barrier heights, and surface shape) in this instance must be such that the more energetic collisions with argon rather than with helium emphasize the "kinetic effect" described below. MOMM calculations predict that **43** and **44** do indeed correspond to energy minima, being nearly identical in terms of steric energy. The barrier between the two minima (calculated to be 0.5 kcal mol^{-1}) should be of low enough energy that argon collisions can convert all of the molecules to a single conformation. As shown in Table IV, the planar conformation **37** of the *tert*-butyl substituent is further confirmed.

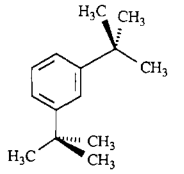
1,3-Di-*tert*-butylbenzene (**45**) represents the most highly substituted and largest molecule in terms of molecular weight examined in these studies. The TOFMS for the 0_0^0 region of the $S_1 \leftarrow S_0$ transition for **45** using 140 psig of helium is presented in Figure 17. We attribute the three features at 37 335.6, 37 388.1, and 37 410.2 cm^{-1} to conformations **46**–**48**, although at this stage we cannot assign conformations to particular transitions. MOMM calculations indicate that **46**–**48** are of nearly equal stability, and hence the unequal intensity of the three transitions may again be due to some kinetic phenomena during the expansion process. Table IV summarizes the results obtained for *tert*-butyl aromatics.



46
0[a]



47
0.30[a]



48
0.15

[a] Steric energy (kcal/mol) (rel).

E. Kinetic Factors in the Expansion Process. Previous papers from our laboratory have addressed the possibility that locally but not globally stable molecular conformations in nonrigid molecules or in van der Waals clusters can be depopulated through collisions in the molecular jet expansion.[7,8,16] In molecules or clusters for which shallow wells and small barriers to conformational changes exist, energetic collisions may, in principle, depopulate local minima in the potential surface in favor of the deeper global ones. The intensity ratios for the 0_0^0 transitions of the various conformers reflect the populations of these conformers which exist at the terminal beam temperature ($T_{\text{trans}} < 1$ K, $T_{\text{rot}} \approx 2$–5 K, and $T_{\text{vib}} \approx 10$–20 K). These populations are not equilibrium populations representative of any particular temperature, however, as they are also affected by the potential surface shape and the kinetic pathway(s) to this terminal temperature.

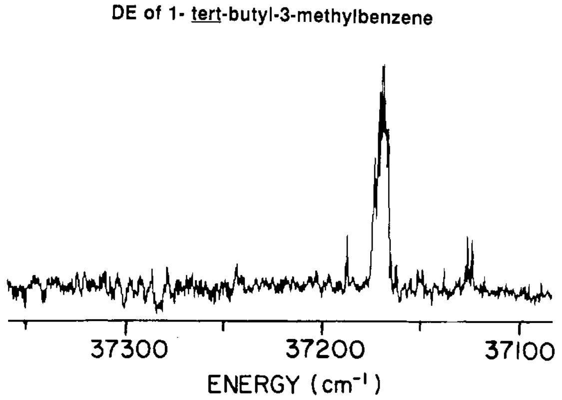


Figure 16. DE spectrum for 1-*tert*-butyl-3-methylbenzene (**42**) obtained by pumping the 37 169.8-cm^{-1} feature in Figure 15a. Resolution is 7.6 cm^{-1}. The absence of a feature to higher energy of the peak at 37 169.8 cm^{-1} helps to preclude the assignment of the 37 169.8-cm^{-1} feature in Figure 15, a and b, as a hot band.

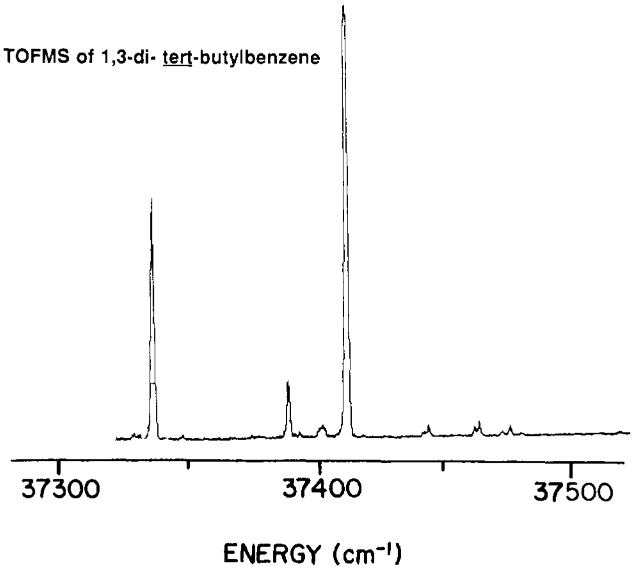


Figure 17. TOFMS of 1,3-di-*tert*-butylbenzene (**45**). The three most intense peaks in the spectrum at 37 335.6, 37 388.1, and 37 410.2 cm^{-1} are assigned to three different spectroscopy origins corresponding to three stable conformations for this molecule.

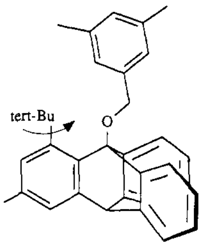
Relative intensities of origins are thus rather unpredictable based on structural expectations or theoretical estimates. Numerous cases exist for which the intensities appear to follow intuition or theory (e.g., 1,3- and 1,4-diethylbenzene,[8] 1-methyl-3-propylbenzene,[5,7] 1-methoxy-3-methylbenzene[16]). On the other hand, for 1,3-di-*tert*-butylbenzene reported herein (Figure 17), expectations of three nearly equally intense 0_0^0 transitions are not met. For cases of "sterically hindered" compounds, e.g., 1-methyl-2-propylbenzene[7] and 1,2-diethylbenzene,[8] equal populations of the various possible conformations are not expected and the 0_0^0 transition intensities are very different. Unequal distribution of conformers in the final expansion equilibrium results in unequal spectroscopic intensities for the different conformations.

To some extent, the expectation or prediction of a kinetic effect is based on ground-state equilibrium distributions calculated from calculated steric energies or heats of formation rather than from any independent experimental data. MOMM calculations allow us to determine the relative populations of the various conformations of a system. If the conformations have free energies within ca. 1 kcal mol^{-1}, they should be populated at room temperature;

however, if the free energy difference is much larger than this, the higher energy forms should be effectively absent from the populated conformations. Thus the calculated energy predictions play a role in the number of conformations *expected* to be observed in our experiments. Hence the identification of a kinetic effect is somewhat tied to calculations of conformational free energies.[4,14] Experimental evidence for a kinetic effect can sometimes be obtained, for example, by performing TOFMS experiments using different expansion gases.

Comparison of Conformational Analysis Capabilities by Jet and Other Spectroscopic Techniques. We emphasize that one of the most fundamental consequences of this work is the spectroscopic observation of specific conformations of simple alkylbenzenes. Because of the low barriers to internal rotation of the substituents in these molecules, previous experimental studies have, with few exceptions, observed only averaged spectroscopic properties for the individual conformations present.[3]

For example, the barrier to rotation about a nonhindered aromatic *tert*-butyl group is quite low, ca. 0.5 kcal mol^{-1}.[3] NMR is not presently capable of observing the individual conformations of such asymmetrically substituted *tert*-butyl systems as reported above. Yamamoto and Ōki[19a,b] reported the first "unambiguous"[19a,b] observation of restricted rotation for an aromatic *tert*-butyl–C_2 group in 1986 for the specially designed, highly hindered molecule **49**. An energy barrier of 9.2 kcal mol^{-1} for rotation about the C_1-*tert*-butyl group was found.[19]



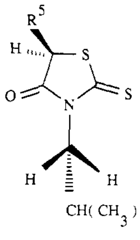
49

The most obvious difference between the Yamamoto and Ōki results[19a,b] and those reported herein is that laser jet spectroscopy is able to observe specific conformations of *unhindered* aromatic substituted *tert*-butyl groups. A more subtle distinction is that the NMR study observed individual spectroscopic signals for the methyl groups of a molecule which has only a *single tert*-butyl conformation.[19] On the other hand, we have observed two or more stable conformations of a specific compound which differ from each other by the arrangement in space of the *tert*-butyl group itself. Thus, we are able to observe spectroscopic properties from the two stable conformations of 1-*tert*-butyl-3-methylbenzene and from the three stable conformations 1,3-di-*tert*-butylbenzene.

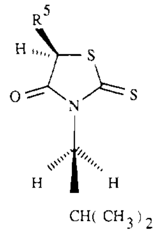
The motion of the isopropyl group and related secondary alkyl substituents (e.g., cyclopropyl, cyclohexyl, carbomethoxy, etc.) has been sufficiently slowed down and detected by NMR spectroscopy, but only in systems for which two adjacent bulky groups significantly increase the barrier to rotation.[3,20] A low-resolution microwave study of meta-substituted isopropylbenzenes has resulted in the observation of two spectroscopically distinguishable band series, one each for the two minimum energy conformations.[18a] On the other hand, we have observed the stable conformations of the simple secondary alkyl-substituted aromatics, 1-methyl-3-isopropylbenzene (two conformations) and 1-ethyl-3-isopropylbenzene (two conformations). Again note the sterically unhindered environment of these substituents.

As found for the *tert*-butyl, isopropyl, and analogous substituents, compounds containing aryl to primary alkyl groups ($ArCH_2R$) have very low barriers to conformational interconversion unless found in sterically encumbered environments. We and others have previously reported the observation of two conformations for both 1,3- and 1,4-diethylbenzene (the anti and syn conformations),[8] propylbenzene (anti and gauche conformations),[7,11,12] and 1-methyl-3-propylbenzene (one anti and two gauche conformations).[7] Low-resolution microwave studies were performed by True et al.[18a] on several ethylbenzenes but could only have observed a single ground-state energy minimum; hence, the crucial experiment of studying molecules which possess two or more stable conformations was not reported. Four origin transitions are observed for 1-ethyl-4-propylbenzene, due to the syn and anti conformations (relative to the perpendicular ethyl substituent) of both the anti and gauche conformations of the propyl substituent **5a**–**5b** and **6a**–**6b**.

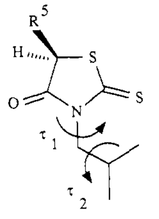
Recently Sandström and co-workers reported one of the very few studies on systems Ar–CH_2R for which R is a bulky alkyl group (in these cases, R = isopropyl and *tert*-butyl, leading to isobutyl and neopentyl substituents).[15a] Using dynamic NMR, they were able to observe the syn and anti conformations (**50** and **51**, respectively) of the 5-alkyl-3-isobutylrhodanines (R^5 = methyl and phenyl). This is equivalent to observing the conformations about τ_1 (cf. **52**). In these cases, however, they did not observe signals for the rotational conformations about the second torsion, τ_2, e.g., **52**. In the current study, two conformations are noted for both 1-isobutyl-2-methylbenzene (**8b** and **8c**) and 1-isobutyl-3-methylbenzene (**8d** and **8e**). The individual conformations depicted by **8** represent torsional isomerism about τ_2. Hence, the laser jet spectroscopy method can observe conformational isomers about both τ_1 and τ_2.



50



51



52

Summary and Conclusions

This study demonstrates the use of supersonic molecular jet laser spectroscopy to establish the existence of various stable conformations of the following types of alkyl-substituted aromatic compounds: those containing aryl to primary alkyl bonds (ethyl, propyl, isobutyl, neopentyl), aryl to secondary alkyl bonds (isopropyl, *sec*-butyl), and aryl to tertiary alkyl bonds (*tert*-butyl). Attention is focused upon two conformational parameters: the position of C_β and C_γ of ArC_α–C_β–C_γ–R (R = H or alkyl) molecular types, i.e., τ_1 and τ_2 in Figure 1.

We have demonstrated the capability of laser jet spectroscopy by investigating substrates in which only small structural features distinguish one conformational energy minimum from another. The observation of two or more 0_0^0 transitions indicates the capability of these high-resolution techniques to observe two (and presumably more) conformations having nearly identical free energy. The most demanding choice, from a structural point of view, would be compounds possessing two or more distant and

---

(19) (a) Yamamoto, G.; Ōki, M. *Tetrahedron Lett.* **1986**, 49. (b) Yamamoto, G.; Ōki, M. *Bull. Chem. Soc., Jpn.* **1986**, *59*, 3597. (c) For an earlier NMR study, Franck et al.[19d] observed ^1H resonances for the individual methyl groups of some 1,8-di-*tert*-butylnaphthalenes at low (<-140 °C) temperature. In these cases, substantial deviation from normal sp^2-hybridization obtains.[19a,b,e] (d) Anderson, J. E.; Franck, R. W.; Mandella, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 4608. (e) Handel, J.; White, J. G.; Franck, R. W.; Yuh, Y. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 3345.

(20) See also: Nilsson, I.; Berg, U.; Sandström, J. *Acta Chem. Scand.* **1984**, *B38*, 491.

noninteracting substituents. Numerous substrates meeting this criterion have been examined.

The ground-state conformational energy minima of various asymmetrically substituted dialkylbenzenes are experimentally established by matching the number of observed 0^0_0 origin transitions to the various "geometrical" possibilities. Thus, the $ArCH_2$–C bond of aromatic to primary alkyl substituents, e.g., ethylbenzene τ_1 (in Figure 1) is perpendicular to the plane of the aromatic ring, and the C–H bond in aryl to secondary alkyl bonds (e.g., in isopropylbenzene) is *in* the plane of the aromatic ring. Similarly, jet spectroscopy has established that one of the methyl groups in *tert*-butylbenzene (an example of an aryl to tertiary alkyl bond containing substrate) is *in* the plane of the aromatic ring.

The second torsion of the aromatic alkyl side chain τ_2 (cf. Figure 1) is also established for a number of compounds, including propylbenzenes and butylbenzenes. In these cases, two ground-state minima are observed for each compound. Unfortunately, information regarding the third torsion $\tau_3(C_\alpha–C_\beta–C_\gamma–C_\delta)$ is not obtained in the only compound possessing a C_δ, namely, butylbenzene. The structural variability at C_δ may be too far removed from the aromatic chromophore in the molecule to allow structural discrimination, even by these sensitive methods.

This work strongly supports our previous conclusions that jet spectroscopy is an excellent technique for the observation and identification of conformations of aromatic molecules which interconvert with very low energy barriers. The experimental observations are complemented by molecular orbital–molecular mechanics (MOMM) calculations which estimate the stabilities of various conformations of these molecules.

Experimental Section

The time-of-flight mass spectrometer was as described elsewhere.[9] The TOFMS experiment used a R.M. Jordan pulsed valve. Both helium and argon were used as carrier gases, as specified for each experiment. All TOFMS experiments were performed at room temperature, and involved one-color two-photon photoionization.

Dispersed emission (DE) experiments were carried out in a fluorescence excitation chamber described previously.[9] f/4 optics were used to collect and focus the emission onto the slits of an f/8 2051 GCA McPherson 1-m scanning monochromator with a dispersion of 2.78 A/mm in third order of a 1200 groove/mm 1.0-μ blazed grating. Expansion of the gas into the chamber was achieved with a Quanta Ray PSV-2 pulsed valve with a 500-μm pinhole located ~1 cm from the laser beam. Samples were placed in the head of the valve and heated to 65–70 °C to achieve a greater concentration in the jet. Helium at 70 psi was used as the carrier gas except as otherwise noted. The alkylbenzenes **7**, **12**, **13**, **15**, **16**, **20**, **21**, **24**, **36**, **40**, **42**, and **45** were purchased from either Aldrich Chemical Co. or Wiley Organics. The purity of these materials was determined by GC and NMR spectroscopy prior to their use. Experimental details for the preparation of **4**, **10**, **11**, **15**, **25**, **26**, and **30** are given in the Supplementary Material.

Empirical force field calculations are performed using the molecular orbital–molecular mechanics (MOMM-85) algorithm of Kao.[14,21] This force field has been specifically parametrized for aromatic ring systems and is known to reproduce experimental geometries and energies. MOMM has also been used to correlate steric energies with the rates of certain aromatic ring additions[22] and pyrolysis reactions.[23] The ground-state calculations are performed using complete geometry optimization to determine the ground-state energy minimum (the stable conformation) and to estimate the potential energy barriers to rotation about the $C_{aromatic}$–C_α and C_α–C_β bonds, i.e., about the torsions τ_1-(C_{ortho}–C_{ipso}–C_α–C_β) and τ_2(C_{ipso}–C_α–C_β–C_γ), respectively.

Acknowledgment. We thank J. Campbell for obtaining the NMR spectra, D. Seal and T. Sinkiewicz for secretarial assistance, R. Ferguson, A. Kassman, B. LaRoy, and C. Lilly for their encouragement and enthusiasm regarding this work, and J. B. Paine III for helpful discussions.

Registry No. 7, 538-93-2; **12**, 1007-26-7; **13**, 104-51-8; **16**, 98-82-8; **20**, 535-77-3; **21**, 4920-99-4; **24**, 135-98-8; **25**, 4481-30-5; **26**, 19262-20-5; **36**, 98-06-6; **40**, 7364-19-4; **42**, 1075-38-3; **45**, 1014-60-4; toluene, 108-88-3; ethylbenzene, 100-41-4; propylbenzene, 103-65-1.

Supplementary Material Available: Experimental details for the preparation of **4**, **10**, **11**, **15**, **25**, **26**, and **30**, including spectroscopic data and elemental analyses for these compounds (5 pages). Ordering information is given on any current masthead page.

---

[21] Kao, J.; Leister, D.; Sito, M. *Tetrahedron Lett.* **1985**, 2403.

[22] Seeman, J. I. *Pure Appl. Chem.* **1987**, *59*, 1661.

[23] Houminer, Y.; Kao, J.; Seeman, J. I. *J. Chem. Soc., Chem. Commun.* **1984**, 1608.

Fourier Transform Mass Spectrometric Generation and Studies of Carboethoxycarbene Anion Radical ($EtOCOCH^{\bullet -}$)

A. Kasem Chowdhury and Charles L. Wilkins*

Contribution from the Department of Chemistry, University of California—Riverside, Riverside, California 92521. *Received August 15, 1988*

Abstract: In contrast to results from flowing afterglow studies, electron attachment with ethyl diazoacetate in a Fourier transform mass spectrometer produces abundant carboethoxycarbene anion radical, $EtOCOCH^{\bullet -}$. Upon collision-induced dissociation, $EtOCOCH^{\bullet -}$ appears to eliminate C_2H_4 via a six-membered transition state yielding an ion with m/z 58. Two resonance structures, a carbon-centered radical anion (I) and an oxygen-centered anion (II), can be considered in order to understand the reactivity of $EtOCOCH^{\bullet -}$. Reactions of $EtOCOCH^{\bullet -}$ with carbonyl compounds and activated olefins can be rationalized by considering the carbon-centered radical anion (I) to make a greater contribution. With use of the bracketing method, the proton affinity of $EtOCOCH^{\bullet -}$ is determined to be 377.2 ± 2 kcal/mol, from which $\Delta H_f(EtOCOCH^{\bullet -}) = -48.5 \pm 3$ kcal/mol was calculated. As a free radical, $EtOCOCH^{\bullet -}$ abstracts $H^\bullet$ atoms from various $H^\bullet$ atom donors. Using such reactions to bracket the hydrogen dissociation energy yields an estimate of $D(EtOCOCH^{-}\text{–}H) \geq 101 \pm 1$ kcal/mol.

Photolytic decomposition of diazo compounds is widely used in synthetic organic chemistry for generating carbene intermediates.[1] Because these latter species possess unfilled electronic valence levels, they are very reactive, and undergo a variety of addition and insertion reactions. Although interest in the structure, stability, and reactivity of carbenes has stimulated extensive studies during the last several decades, the anionic analogues of carbenes have received attention only recently.

Both gas-phase[2,3] and condensed-phase[4,5] studies suggest that

---

[1] (a) Jones, M., Jr.; Moss, R. A. *Carbenes*; Wiley: New York, 1973; Vol. I and II. (b) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.

[2] Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731–3732.

[3] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498.

0002-7863/89/1511-3150$01.50/0