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"A STUDY OF NON RIGID AROMATIC MOLECULES BY SUPERSONIC MOLECULAR JET SPECTROSCOPY. OBSERVATION AND SPECTROSCOPIC ANALYSIS OF THE STABLE CONFORMATIONS OF VARIOUS ALKYLBENZENES"

by

J.I. Seeman, H.V. Secor, P.J. Breen, V.H. Grassian, E.R. Bernstein

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July, 1988

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

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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/mole, can be isolated in the supersonic jet expansion. Each observed conformation exhibits its own spectroscopic origin ($S_1 \leftarrow S_0$ transition) in a 2-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 mimima a molecule possesses.

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 (c.f. Chart 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 (c.f. 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 $0° < \tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta) < 90°$.

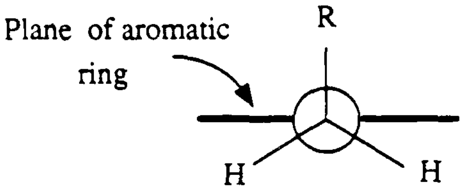
In this report, the two-color time of flight mass spectra (TOFMS) and dispersed emission (DE) spectra of several alkyl substituted benzenes (c.f. Chart I) are presented and analyzed in terms of the individual ground state conformations of these non-rigid molecules.[10] In particular, we consider the 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? and (d) in addition to observing different conformations, will this technique provide an experimental determination of their geometries?

RESULTS AND DISCUSSION

A. Results of Previous Jet Studies

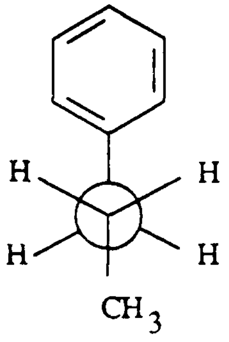
The barrier to internal rotation of the methyl group in toluene is extremely small due, in part, to the barrier's six-fold symmetry. Hence, assignment of a stable conformational form for this molecule is not meaningful.[6,13,14] Our observation of two 0_0^0 transitions in the TOFMS for both 1,3-diethylbenzene 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 is a global energy minimum.[8]



1a, $R = CH_3$

b, $R = CH_3CH_2$

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., $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta) = 90°$ as illustrated by **1b** for both **2** and **3**.



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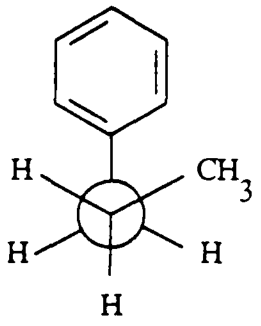


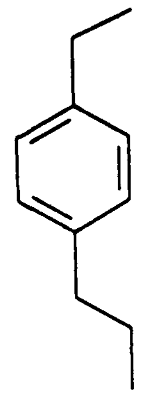
3

0.39

Steric Energy (kcal mol^{-1}) (rel)

B. Compounds Containing an Aryl to a Primary Alkyl Bond ($ArCH_2R$)

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_2R 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 specifing the relative disposition of the two substituents with respect to each other, the second descriptor specifing 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 37369.1, 37372.7 and 37496.7, 37497.3 cm^{-1}). The third doublet at ca. 37548 cm^{-1} is assigned as a torsional motion of the substituent group in accord with previous work.[5-8]



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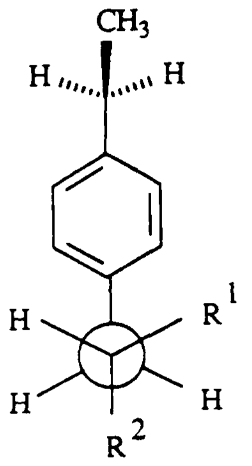

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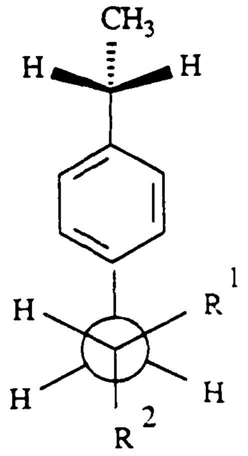
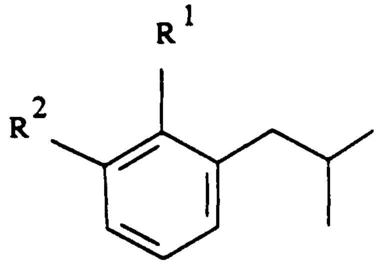


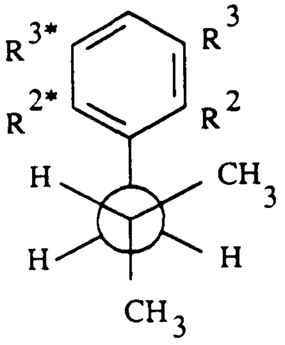
6

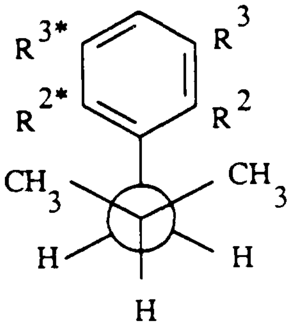
a, $R^1 = H$, $R^2 = CH_3$

b, $R^1 = CH_3$, $R^2 = H$

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 37517.8 cm^{-1}. Two weak features, assigned as isobutyl torsions, occur at 37551.4 and 37559.6 cm^{-1}. Comparison of this spectrum to that of propybenzene[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**.







7, $R^1 = R^2 = H$
10, $R^1 = H$, $R^2 = CH_3$
11, $R^1 = CH_3$, $R^2 = H$

8

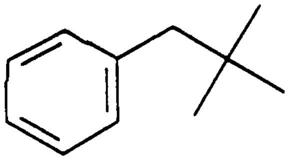
9

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, $R^{3*} = CH_3$, $R^2 = R^{3*} = R^3 = H$

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 Fig. 4 evidences two origins, at 36965.1 and 37023.0 cm^{-1} (with 1e ← 1e ring methyl torsions occurring ~3 cm^{-1} to lower energy of each origin[4,7]) 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 $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta) = 90°$ for the isobutyl substituent.[15]

The TOFMS of 1-isobutyl-2-methylbenzene **(11)** (Figure 5) contains two origins at 37036.0 and 37171.8 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. 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, $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta) = 90°$ 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 $C_\alpha-C_\beta$ bond (τ_2) and has $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta)$ = ca. 90°.



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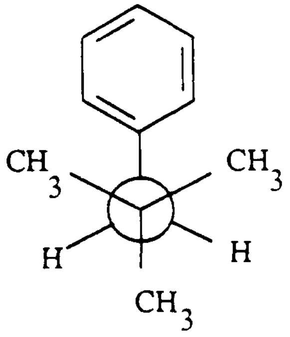


12a

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 37581.8 cm^{-1}, with what appears to be a weaker origin to lower energy, at 37578.0 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 37581.8 cm^{-1} is indeed due to a single molecular conformation, it is most likely associated with the extended conformation **14aa** (Chart 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.[5-8,14] The assignment is consistent with our previous observations that the anti conformer is energetically favored over the gauche. The less intense origin at 37578.0 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}.[3,10] 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 37578.0 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}.

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 **14ag** and gauche/anti **14ga**) expected based on simple conformational analysis concepts or on our MOMM calculations (Chart II). Previous papers from our laboratory have addressed the possibility that local, but not global, stable molecular conformations in non-rigid 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[16]), not all of the conceivable locally stable orientations of the non-rigid 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.

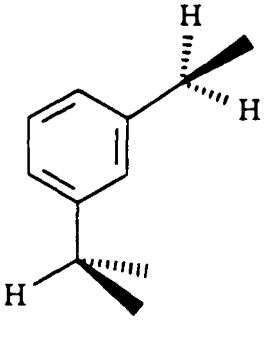
C. Compounds Containing an Aryl to a Secondary Alkyl Bond ($ArCHR^1R^2$)

Isopropylbenzene **(16)** is the prototype of molecules 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 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 37668.5 cm^{-1} and a much weaker feature at 37710.0 cm^{-1}, the latter attributed to torsional motion of the isopropyl group.[5-8] Chart 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**, Chart IIB) and 3-ethyl-1-isopropylbenzene (**21**, Chart IIC).

The TOFMS for 1-isopropyl-3-methylbenzene (**20**), presented in Fig. 9, contains two origins: the doublet at ca. 37165 cm^{-1} and a less intense feature at 37156.0 cm^{-1}. Meta-substituted toluenes have been observed in the past[7,8] 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 37156.0 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 37191.8 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** (Chart 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 (Chart 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 37226.6 and 37264.8 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 in the meta position then yields conformers **22** and **23**. This conclusion agrees with our MOMM calculations and with the other literature data which likewise predict **17** to be the stable conformation for isopropylbenzene.



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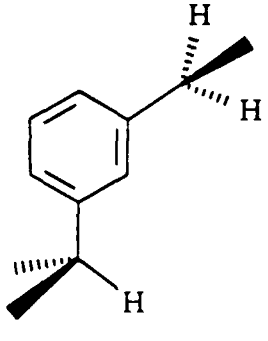
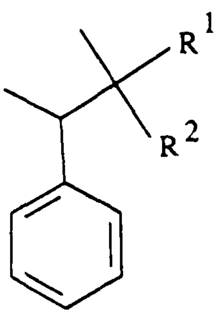


23

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.

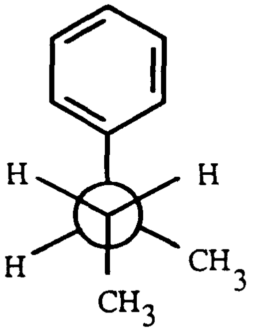


24, $R^1 = R^2 = H$

25, $R^1 = CH_3$, $R^2 = H$

26, $R^1 = R^2 = CH_3$

The TOFMS of <u>sec</u>-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 37627.1 cm^{-1}. The weaker feature occurring at 37661.3 cm^{-1} is presumably due to torsional motion of the alkyl group as discussed earlier. Only a single conformation for <u>sec</u>-butylbenzene is observed. As a first approximation, $\tau_1(C_{ortho}-C_{ipso}-C_{\alpha}-H_{\alpha})$ should equal 0° for <u>sec</u>-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 <u>sec</u>-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 <u>sec</u>-butylbenzene observed in the jet corresponds to **29**.



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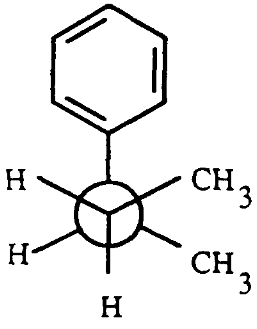

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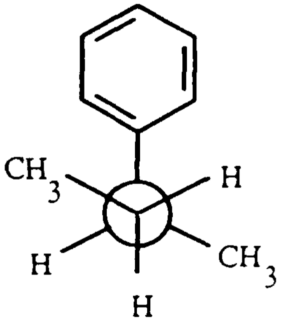
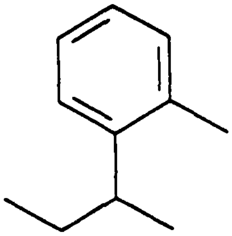


29

0

Steric Energy (kcal mol^{-1}) (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**.



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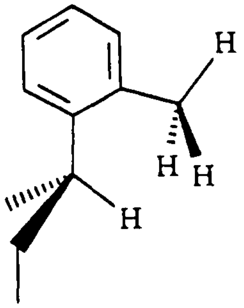
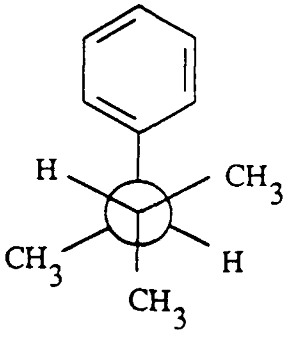


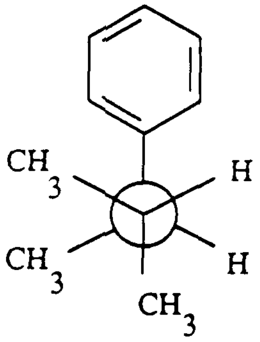
31

(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 37556.6 cm^{-1} and 37585.9 cm^{-1}. The origin to the red (low energy) is approximately 10% the intensity of the second origin. We tentatively assign the 37556.6 cm^{-1} origin as **33** and the 37585.9 cm^{-1} origin as **32** based on the relative intensities of the two origins and the calculated relative stabilities.



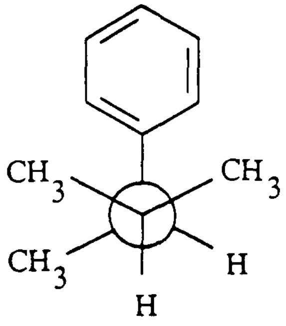
32

0



33

0.95

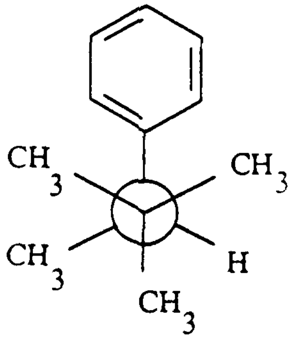


34

1.3

Steric Energy (kcal mol^{-1}) (rel)

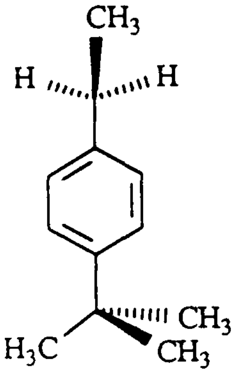
(1,2,2-Trimethylpropyl)benzene (**26**) has only one staggered conformation, namely **35**, and its TOFMS shows a single origin at 37585.8 cm^{-1}.



35

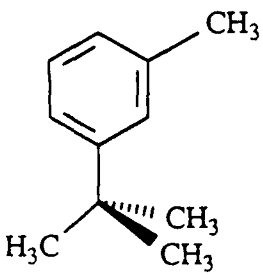
D. Compounds Containing an Aryl to a Tertiary Alkyl Bond ($ArCR^1R^2R^3$)

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 37696.2 cm^{-1}, which means that only one of the three postulated conformations (planar **37**, perpendicular **38**, gauche **39**; c.f. Chart IV) is an energy minimum, and therefore only one of these species 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 are in agreement as to the number and position of potential minima on those two surfaces, we conclude that these determinations are valid.

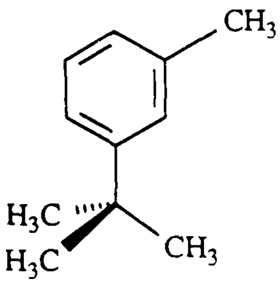


41

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 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 37136 cm^{-1}. Figure 15a also displays two other intense features at 37165.0 and 37169.8 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.



43

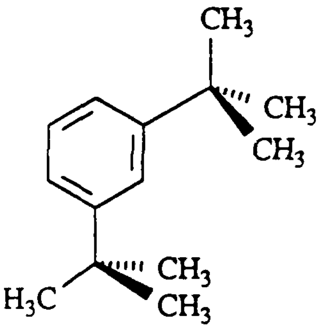


44

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 37169.8 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 37169.8 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.

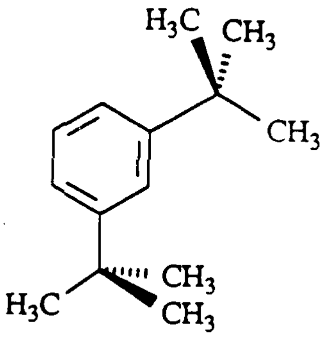
These three results (TOFMS, DE, and rigid rotor calculations) can be rationalized by assigning the feature in question as due to a second conformation of **42** which can be depopulated in the argon expansion. The conformational energy balance (well depth, barrier heights, and surface shape) in this 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 Chart IV, the planar conformation **37** of the <u>tert</u>-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 37335.6, 37388.1 and 37410.2 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. Chart IV summarizes the results obtained for tert-butylaromatics.



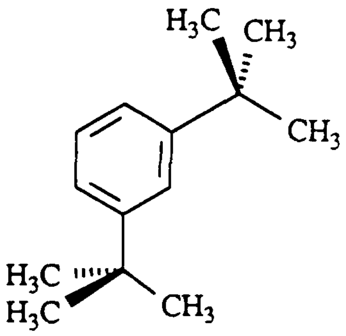
46

0



47

0.30



48

0.15

Steric Energy (kcal mol^{-1}) (rel)

E. Kinetic Factors in the Expansion Process

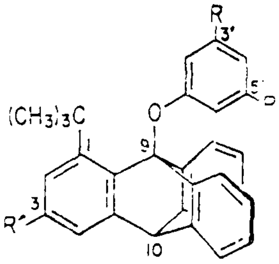
Previous papers from our laboratory have addressed the possibility that locally but not globally stable molecular conformations in non-rigid molecules or in van der Waals clusters can be depopulated through collisions in the molecular jet expansion.[7,8] In molecules or clusters for which shallow wells 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. Thus, w have reported two cases of "sterically hindered" compounds, namely 1-methyl-2-propylbenzene[7] and 1,2-diethylbenzene[8] in which one of the conceivable locally stable orientations of the non-rigid moiety is not sufficiently populated in the expansion gas to generate an absorption spectrum. This 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. 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 reported the first observation of restricted rotation for an aromatic *tert*-butyl 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]



$R=CH_3$, $R'=C(CH_3)_3$

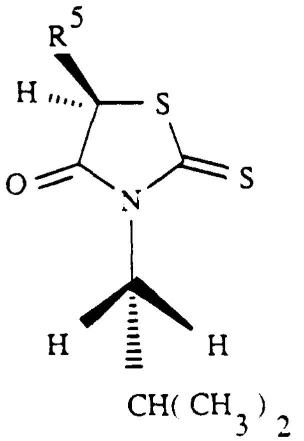
49

The most obvious difference between the Yamamoto and Ōki results[18] 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 the two stable conformations of 1-tert-butyl-3-methylbenzene, and 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 (2 conformations) and 1-ethyl-3-isopropylbenzene (2 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 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 Sandstrom and coworkers reported one of the very few studies on systems $Ar\text{-}CH_2R$ for which R is a bulky alkyl group (in these cases, R = isopropyl and <u>tert</u>-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 (c.f. **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.



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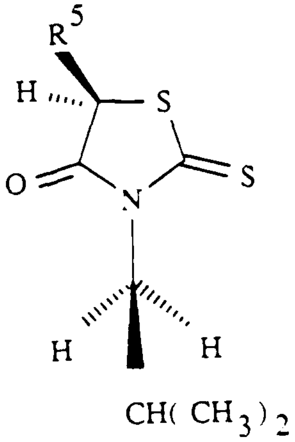
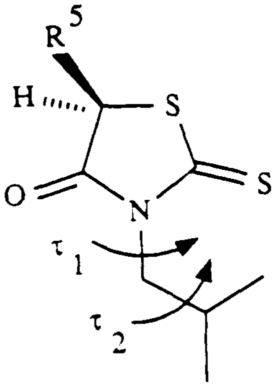


51



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 primarly alkyl bonds (ethyl, propyl, isobutyl, neopentyl), aryl to secondary alkyl bonds (isopropyl, <u>sec</u>-butyl) and aryl to tertiary alkyl bonds (<u>tert</u>-butyl). Attention is focused upon two conformational parameters: the position of C_β and C_γ of $ArC_\alpha\text{-}C_\beta\text{-}C_\gamma\text{-}R$ (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 non-interacting 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 $ArCH_2\text{-}C$ 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 <u>in</u> the plane of the aromatic ring. Similarly, jet spectroscopy has established that one of the methyl groups in tert-butylbenzene (an example of a 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 (c.f. 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.[8] 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.[8] f/4 optics were used to collect and focus the emission onto the slits of an f/8 2051 GCA McPherson 1 meter 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, 12-14, 16, 21-22, 24, 36, 40, 42 and 45** were purchased from either Aldrich Chemical Company 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, 28, 30,** and **34** 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 $C_{aromatic}-C_{\alpha}$ and $C_{\alpha}-C_{\beta}$ bonds, i.e., about the torsions $\tau_1(C_{ortho}-C_{ipso}-C_{\alpha}-C_{\beta})$ and $\tau_2(C_{ipso}-C_{\alpha}-C_{\beta}-C_{\gamma})$, 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.

Supplementary Material Available: Experimental details for the preparation of **4, 10, 11, 15, 28, 30,** and **34,** including spectroscopic data and elemental analyses for these compounds (six pages). Ordering information is given on any current masthead page.

Chart I. Substituent Patterns for Substrates Examined in This Work

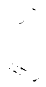
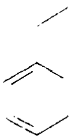
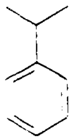
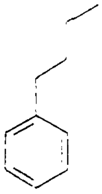
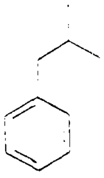
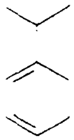
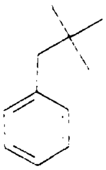
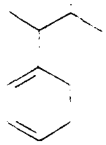
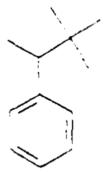
	Aryl-to-Alkyl Bond Type		
number of atoms in substituents	primary Ar-CH$_2$R	secondary Ar-CHR^{1}R^2	tertiary Ar-CR^{1}R^{2}R^3
C_1			
C_2			
C_3			
C_4	 		
C_5			
C_6			

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

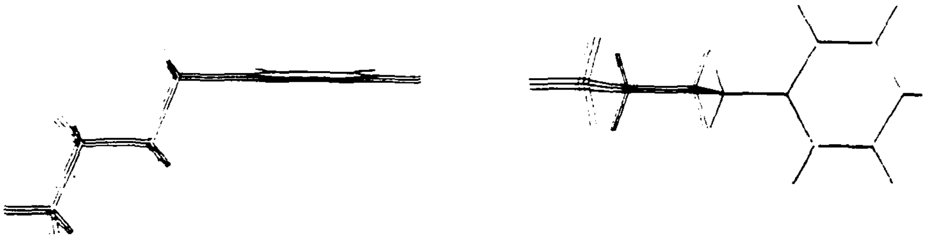
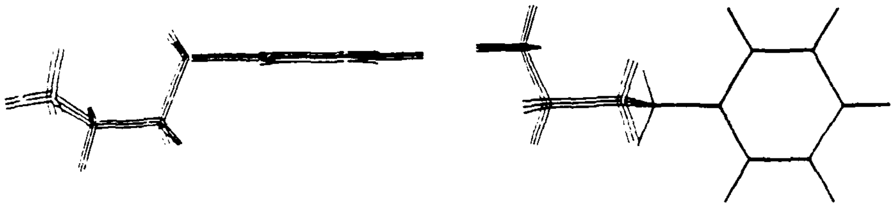
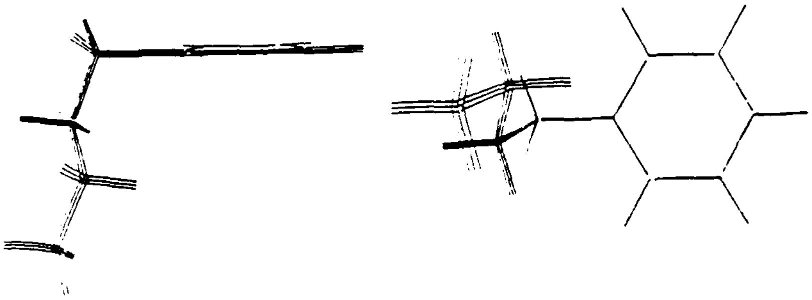
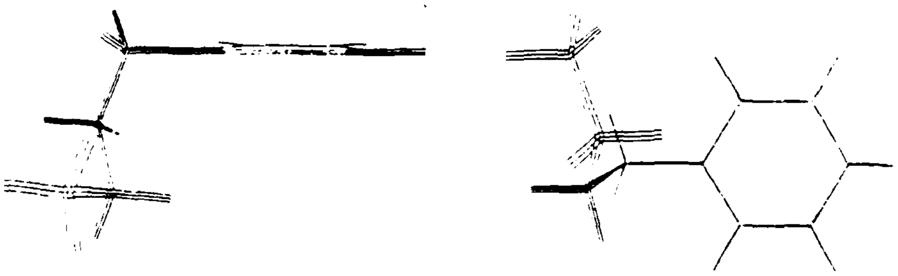
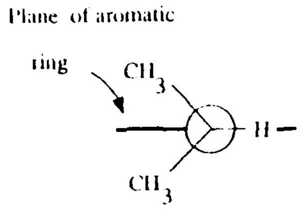
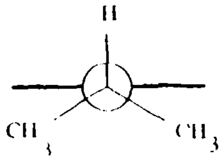
conformation	SE (kcal/mol) (rel)	
14aa	0	
14ag	1.85	
14ga	1.30	
14gg	2.02	

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



17



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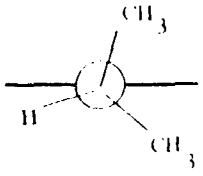


19

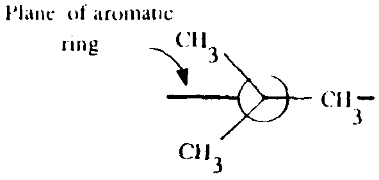
compound	number of conformations			
	predicted[a]			
	17	**18**	**19**	
	planar[b]	perpendicular[b]	gauche[b]	observed[c]
isopropylbenzene (**16**)	1	1	1	1
1-isopropyl-3-methylbenzene (**20**)	2	1	2	2
1-ethyl-3-isopropylbenzene (**21**)	2	2	4	2

[a] Based on counting all possible molecular conformations having the specific substituent conformation depicted, but counting degenerate conformations only once.

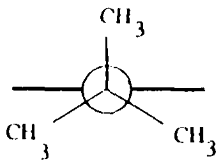
[b] This term refers to the relative position of the α-H and the plane of the aromatic ring.

[c] Number of origin transitions observed by TOFMS. See text for additional discussion.

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



37



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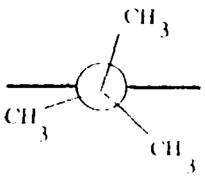


39

compound	number of conformations			
	predicted[a]			
	37	**38**	**39**	
	planar	perpendicular	gauche	observed[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 Captions

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

Figure 2 TOFMS of the 0_0^0 region of 1-ethyl-4-propylbenzene **(4)**. The spectrum consists of four origins at 37369.1, 37372.7 and 37496.7, 37497.3 cm^{-1}, corresponding to four stable conformations for this molecule (see text).

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 37517.8 cm^{-1}. The weak features at 37551.4 and 37559.6 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 36965.1 and 37023.0 cm^{-1}. The peaks occurring 3 cm^{-1} lower in energy than these origins are due to ring methyl torsions.

Figure 5 TOFMS of the 0_0^0 region of 1-isobutyl-2-methylbenzene **(11)**. Two origins are observed in the spectrum at 37036.0 and 37171.8 cm^{-1}.

Figure 6 TOFMS of the 0_0^0 region of neopentylbenzene **(12)**. The spectrum shows only one origin at 37533.6 cm^{-1}. Weaker features, higher in energy to the origin, are attributed to low frequency torsional motions of the neopentyl group.

Figure 7 TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of butylbenzene **(13)**. The intense feature at 37581.8 cm^{-1} is assigned to the staggered, all anti conformation of the butyl group **(14aa)**. The weaker feature at 37578.0 cm^{-1} is also assigned as a separate origin, corresponding to **14ag**.

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 37668.5 cm^{-1}. The weaker feature at 37710.0 cm^{-1} is attributed to torsional motion of the isopropyl group.

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 37165.9 cm^{-1} is an origin which forms a doublet with the peak at 37164.0 cm^{-1}. This latter peak is attributed to the 1e ← 1e internal rotational transition of the ring methyl rotor. The weaker peak at 37156.0 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 37226.6 and 37264.8 cm^{-1}, help identify the stable conformation of the isopropyl group as **17**, as outlined in the text.

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 37627.1 cm^{-1}. The weak feature at 37661.3 cm^{-1} is attributed to torsional motion of the sec-butyl group.

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).

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 37696.2 cm^{-1} and is indicative of a single stable molecular conformation.

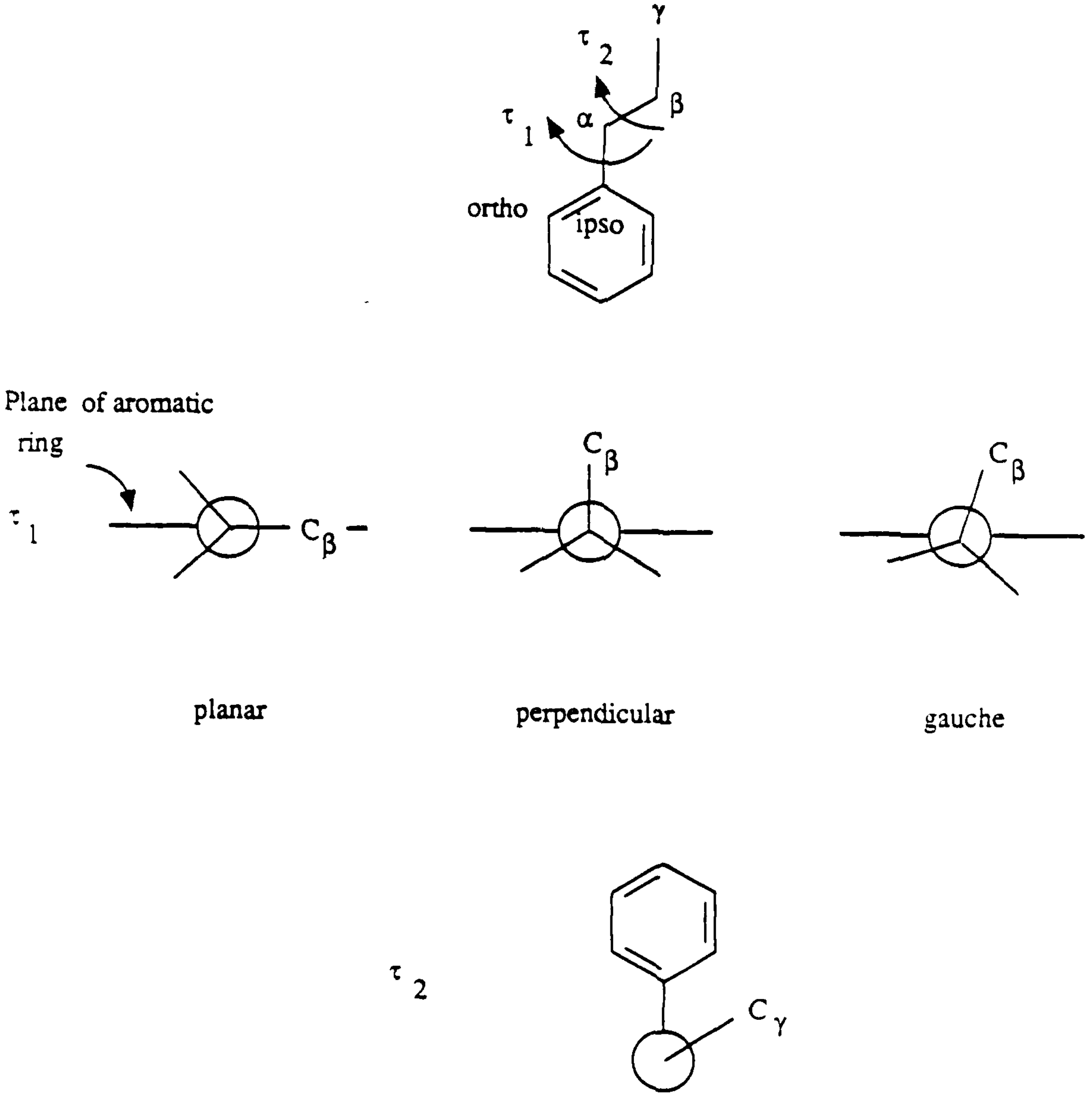
Figure 14 TOFMS of the 0^0_0 region of the $S_1 \leftarrow S_0$ transition of 1-*tert*-butyl-4-ethylbenzene **(40)**. The fact that this spectrum contains only one origin at 37,142 cm^{-1} identifies the stable molecular conformation of the *tert*-butyl group as **31**.

Figure 15 TOFMS of the 0^0_0 region of the $S_1 \leftarrow S_0$ transition of 1-*tert*-butyl-3-ethylbenzene **(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 37137.0 and 37169.8 cm^{-1} are origins for two different molecular conformations. The 37169.8 cm^{-1} peak disappears in Figure 15c due to a kinetic effect discussed in the text.

Figure 16 DE spectrum for 1-*tert*-butyl-3-methylbenzene **(42)** obtained by pumping the 37169.8 cm^{-1} feature in Figure 15a. Resolution is 7.6 cm^{-1}. The absence of a feature to higher energy of the peak at 37169.8 cm^{-1} helps to preclude the assignment of the 37169.8 cm^{-1} feature in figures 15a and 15b as a hot band.

Figure 17 TOFMS of 1,3-di-*tert*-butylbenzene **(45)**. The three most intense peaks in the spectrum at 37335.6, 37388.1 and 37410.2 cm^{-1} are assigned to three different spectroscopic origins corresponding to three stable conformations for this molecule.

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



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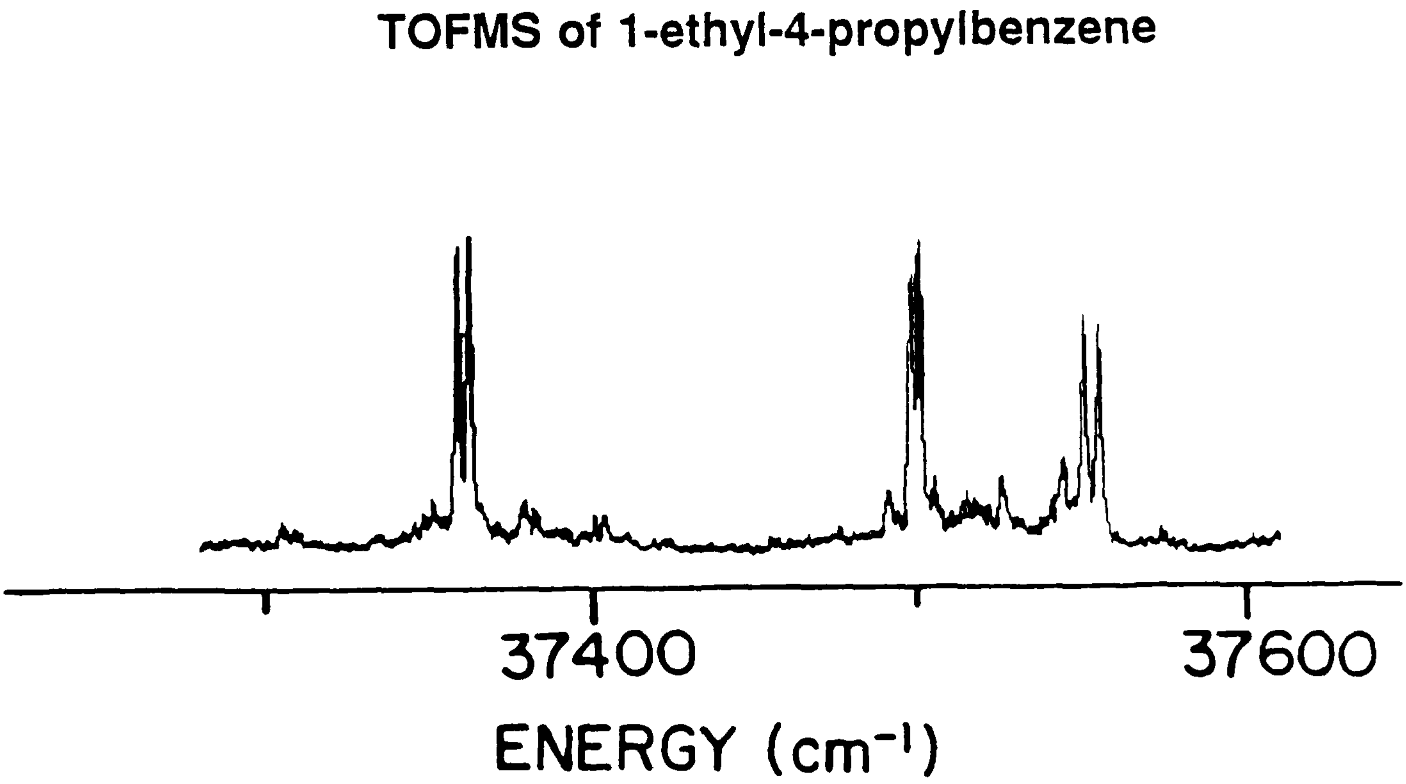

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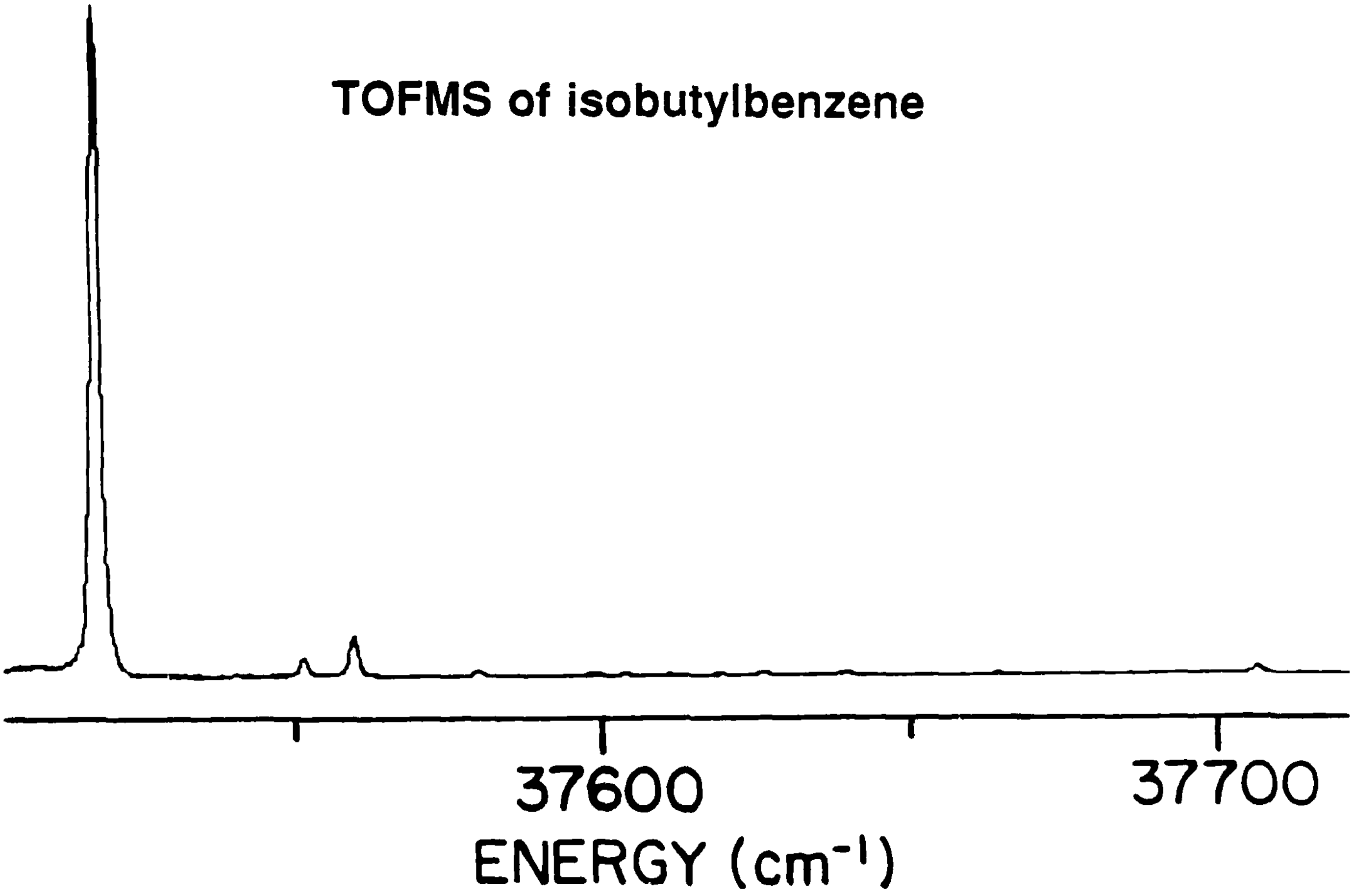

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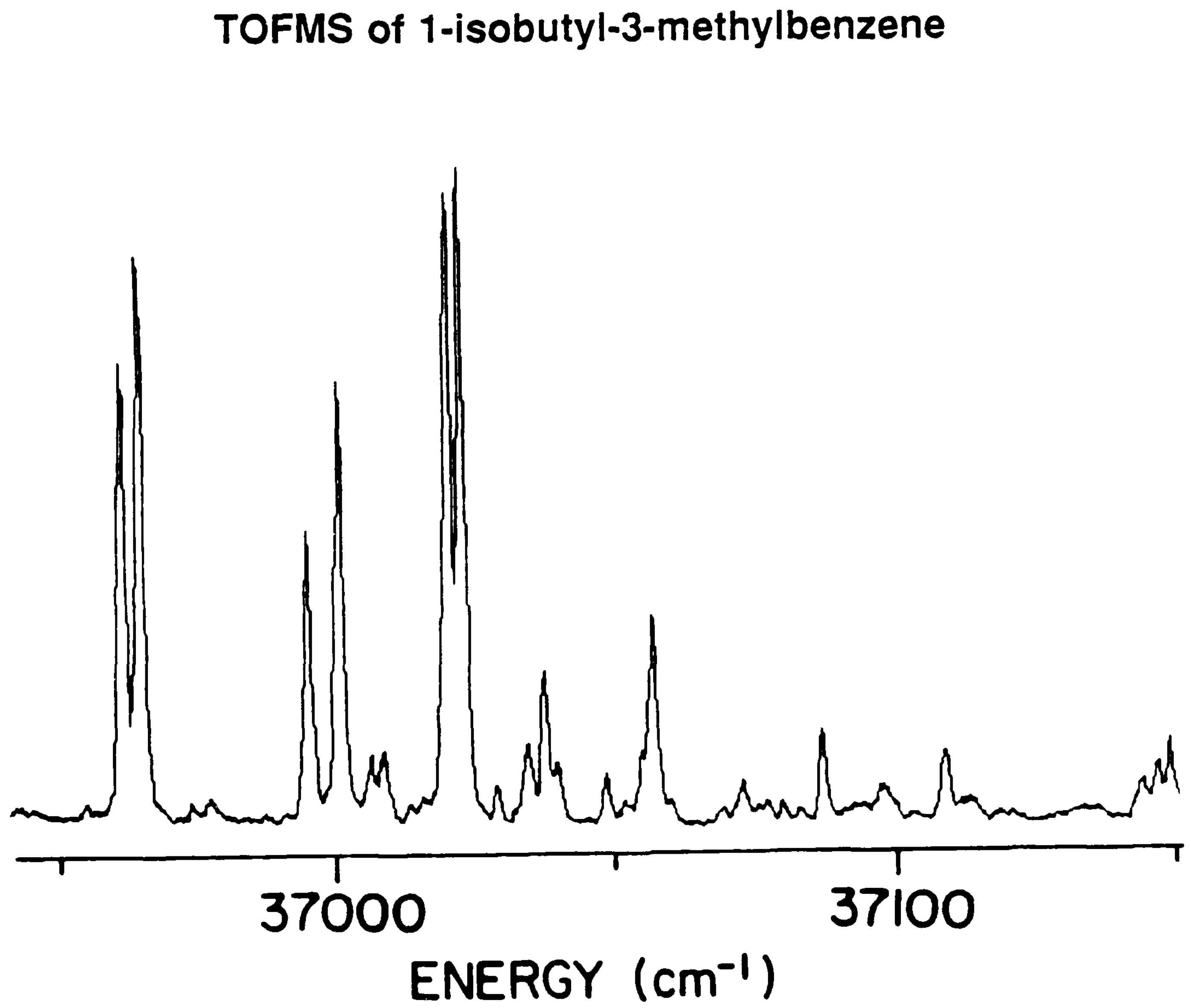

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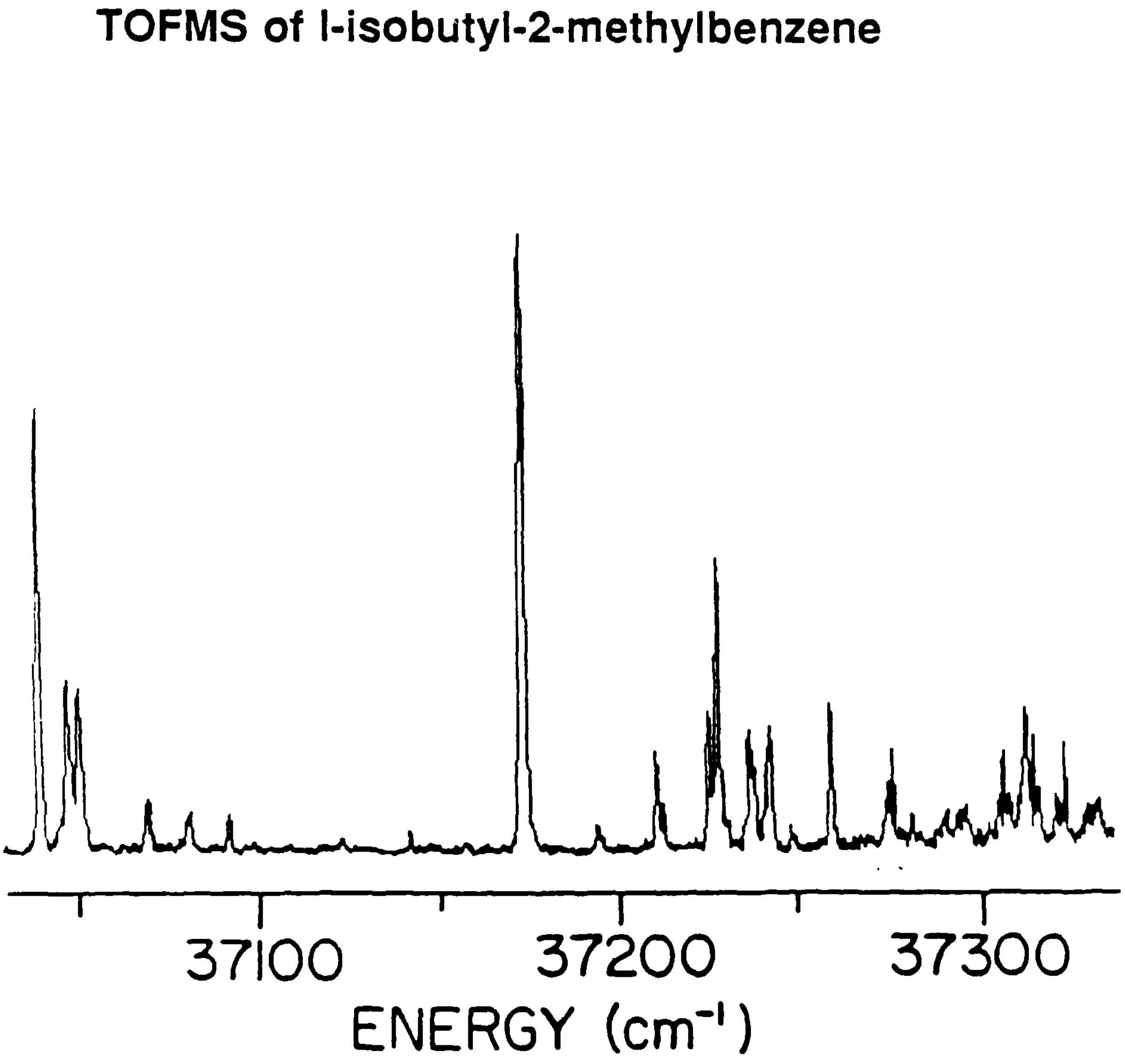

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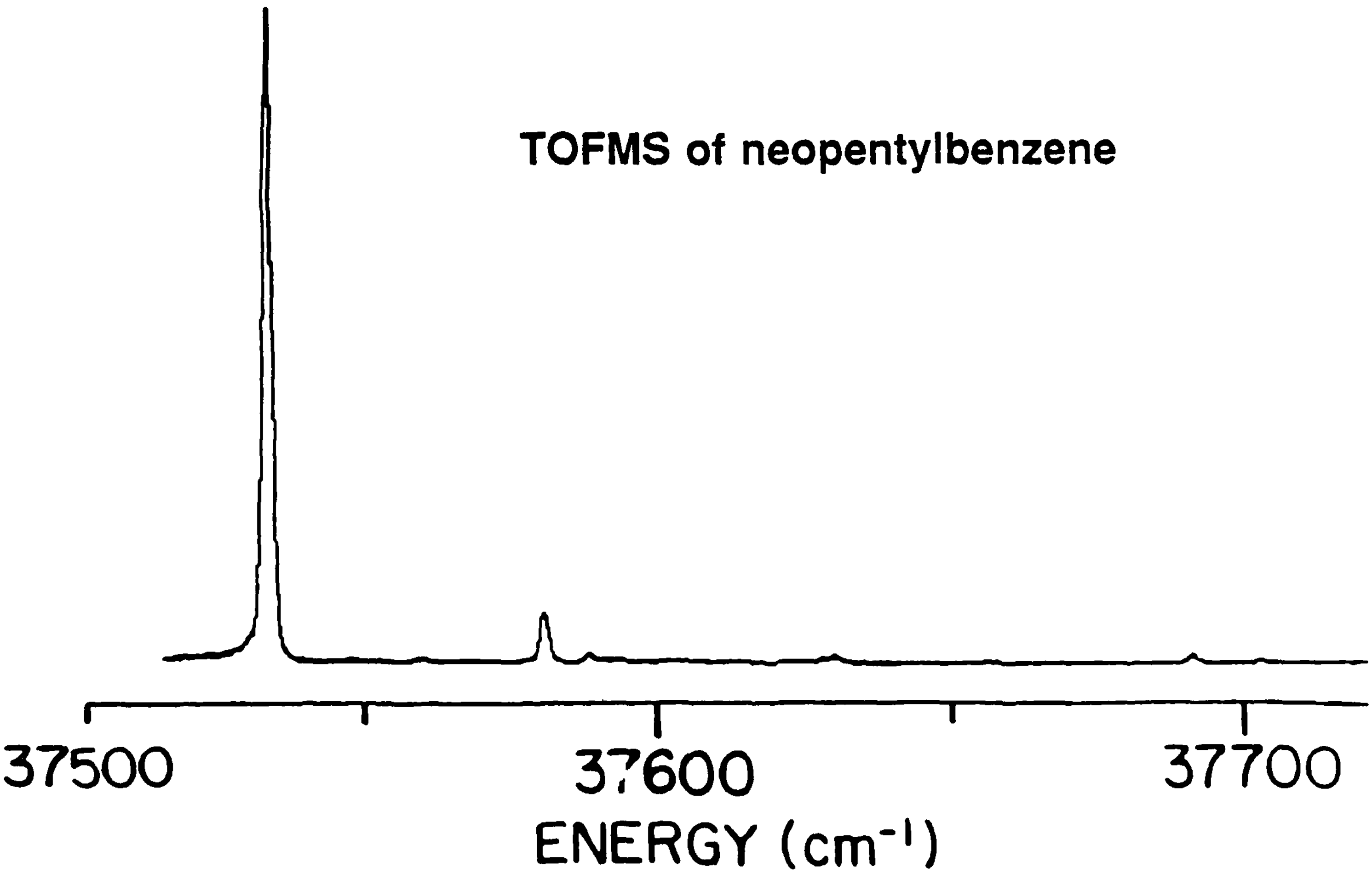

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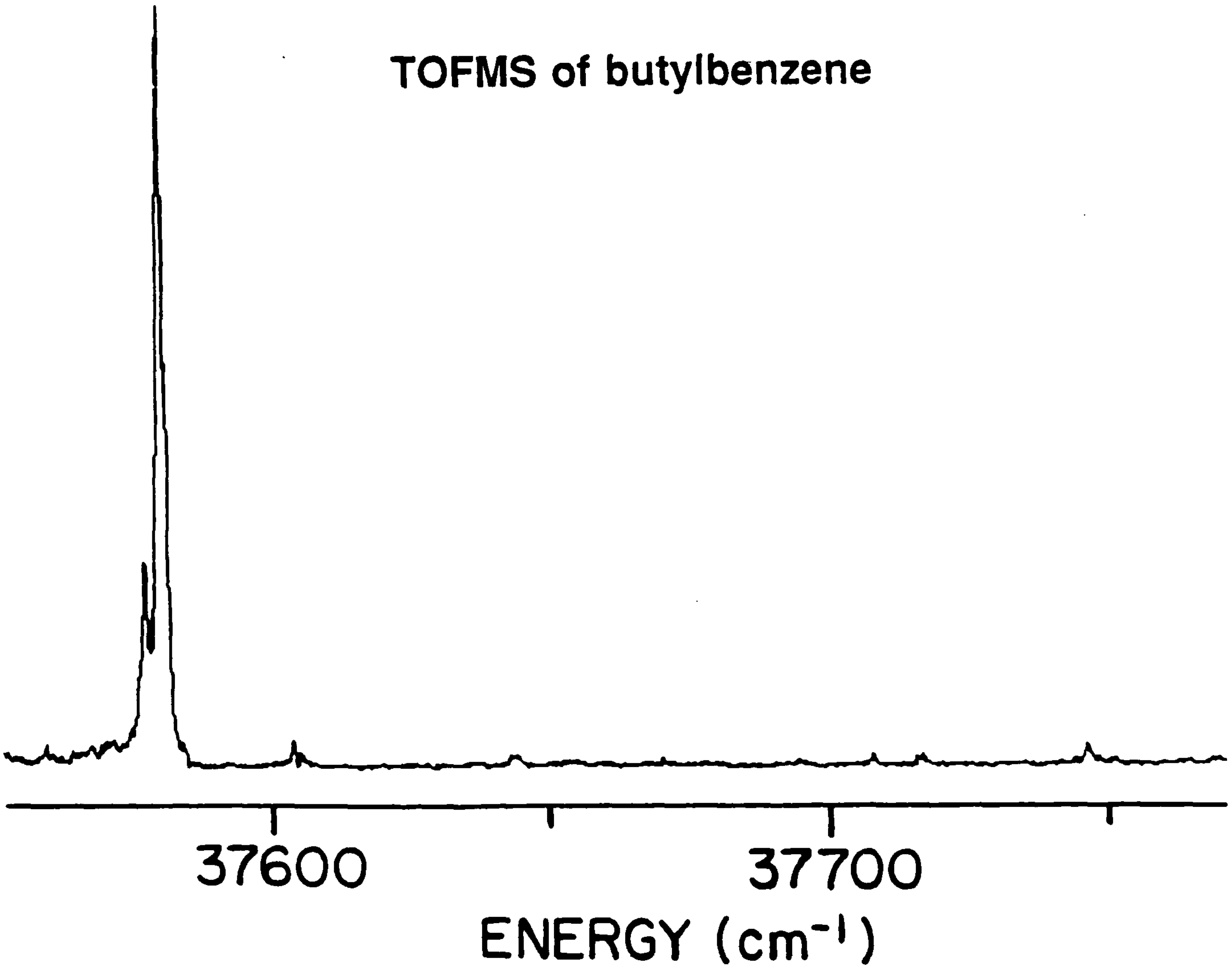

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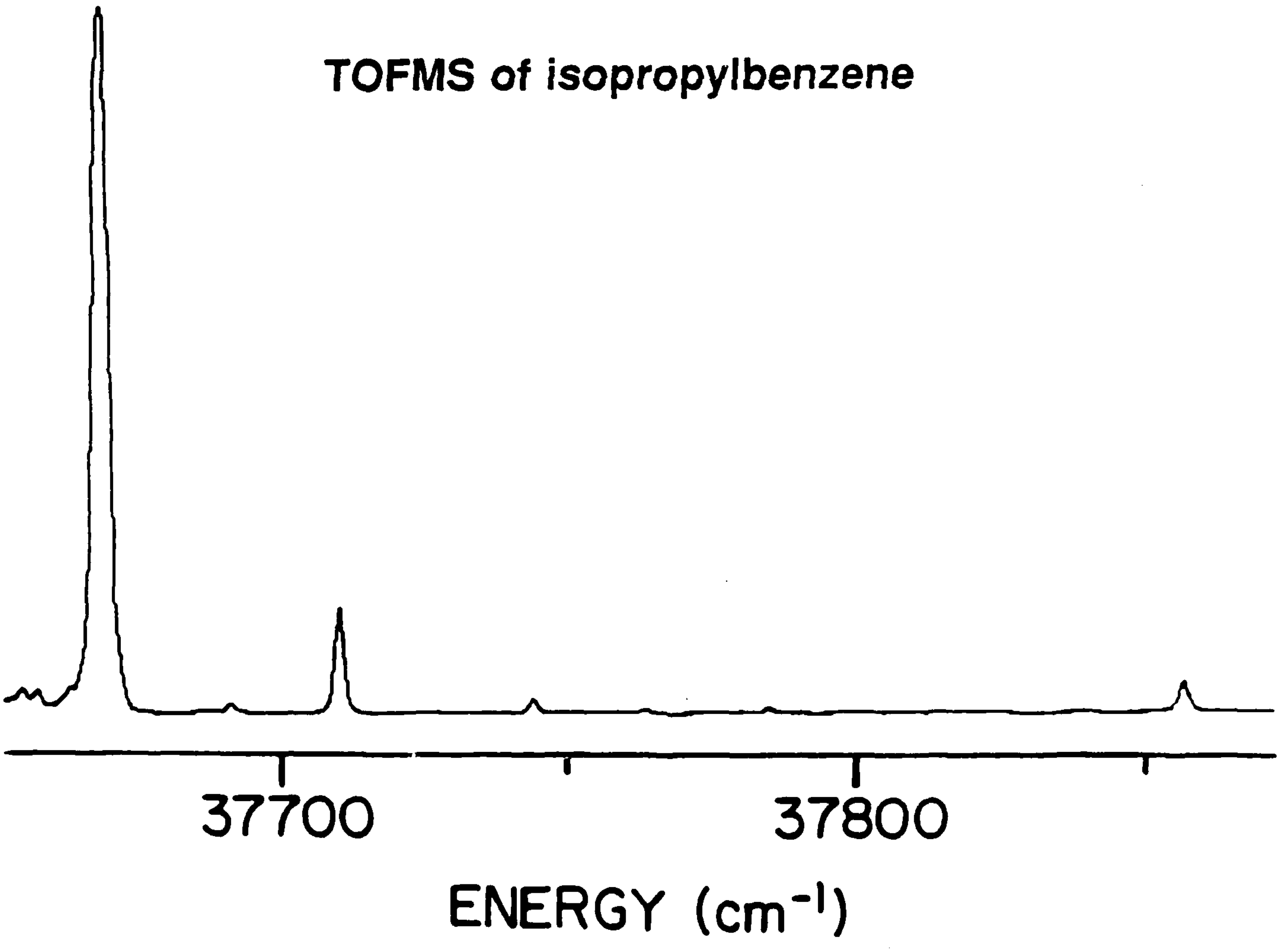

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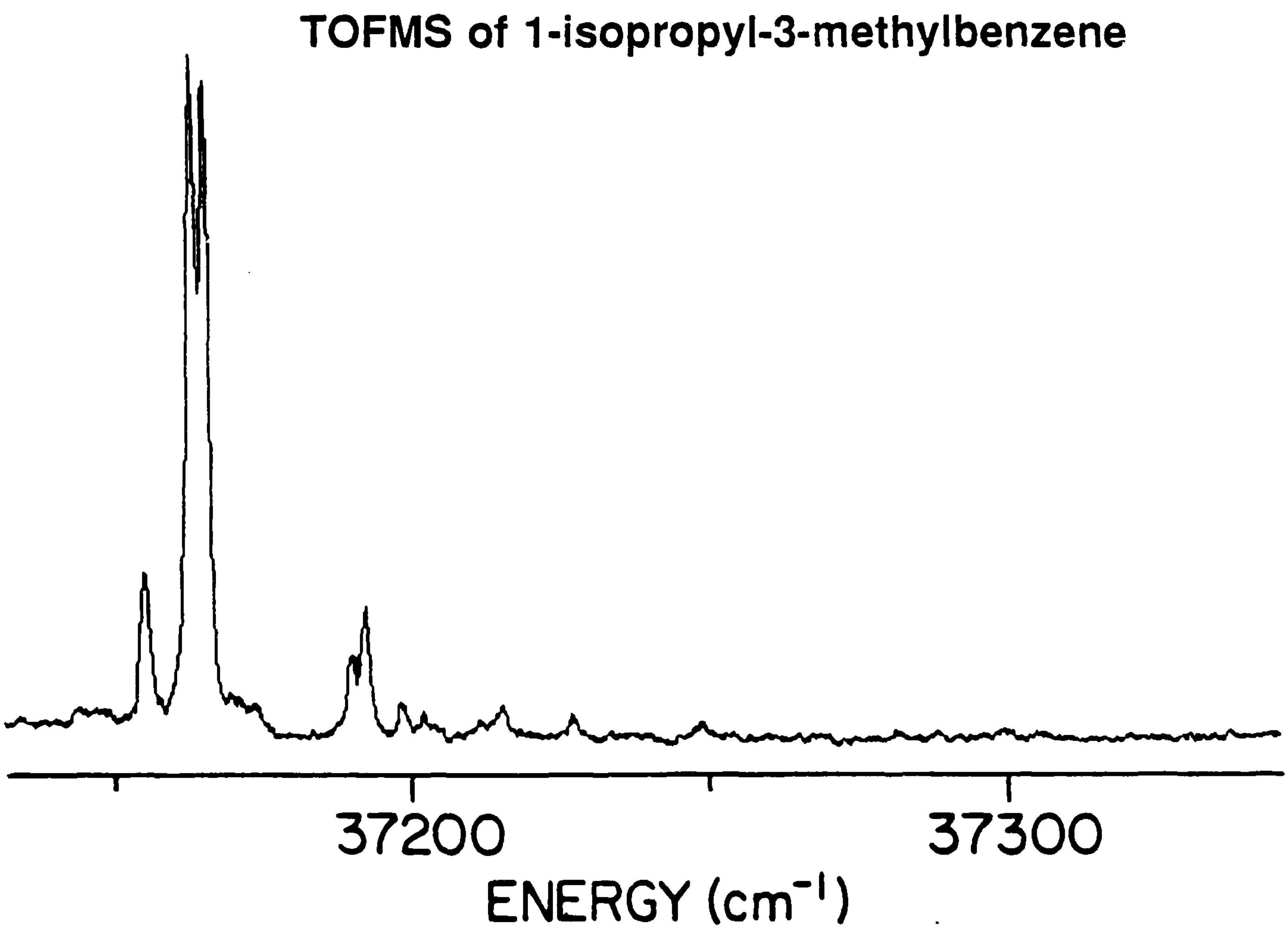

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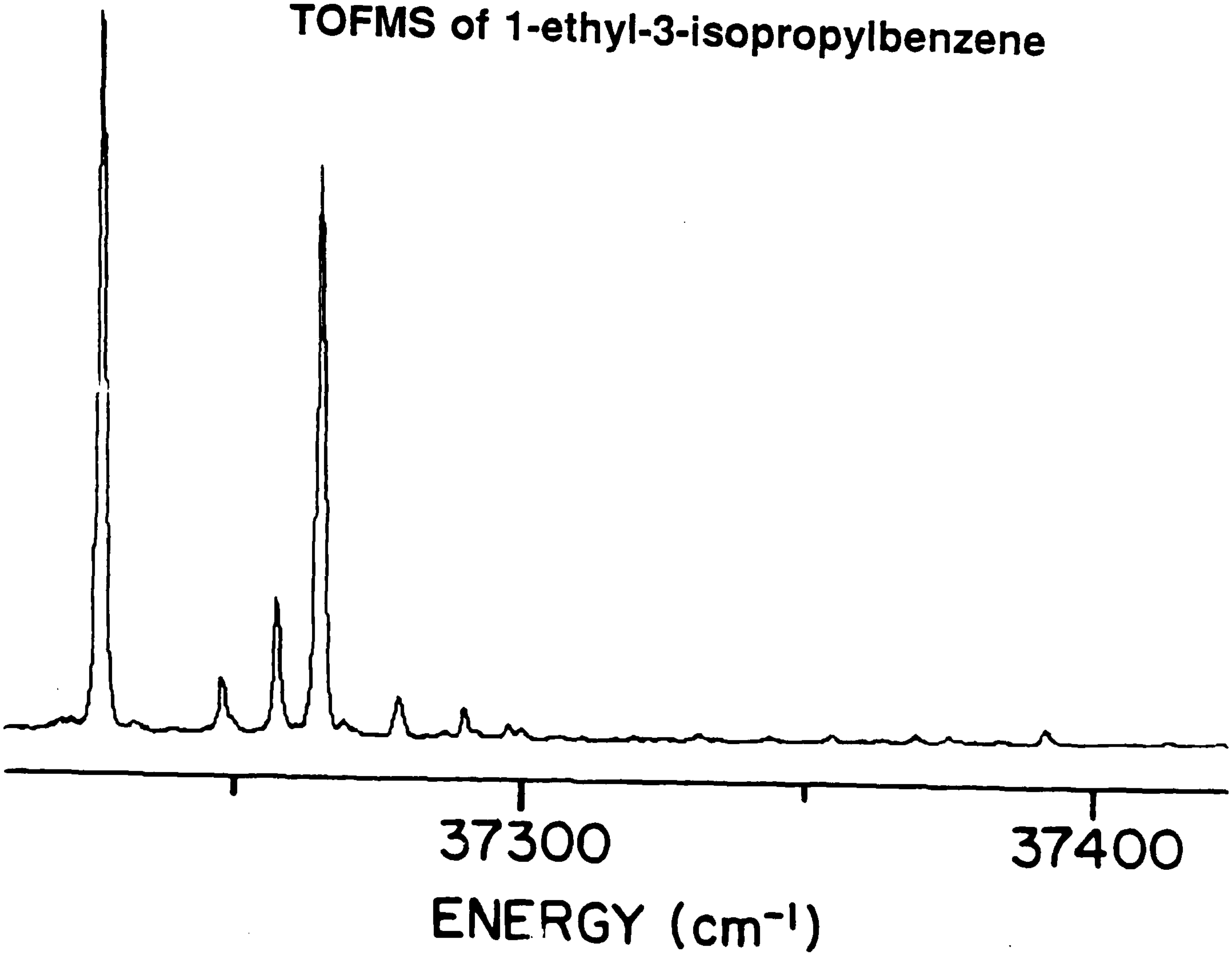

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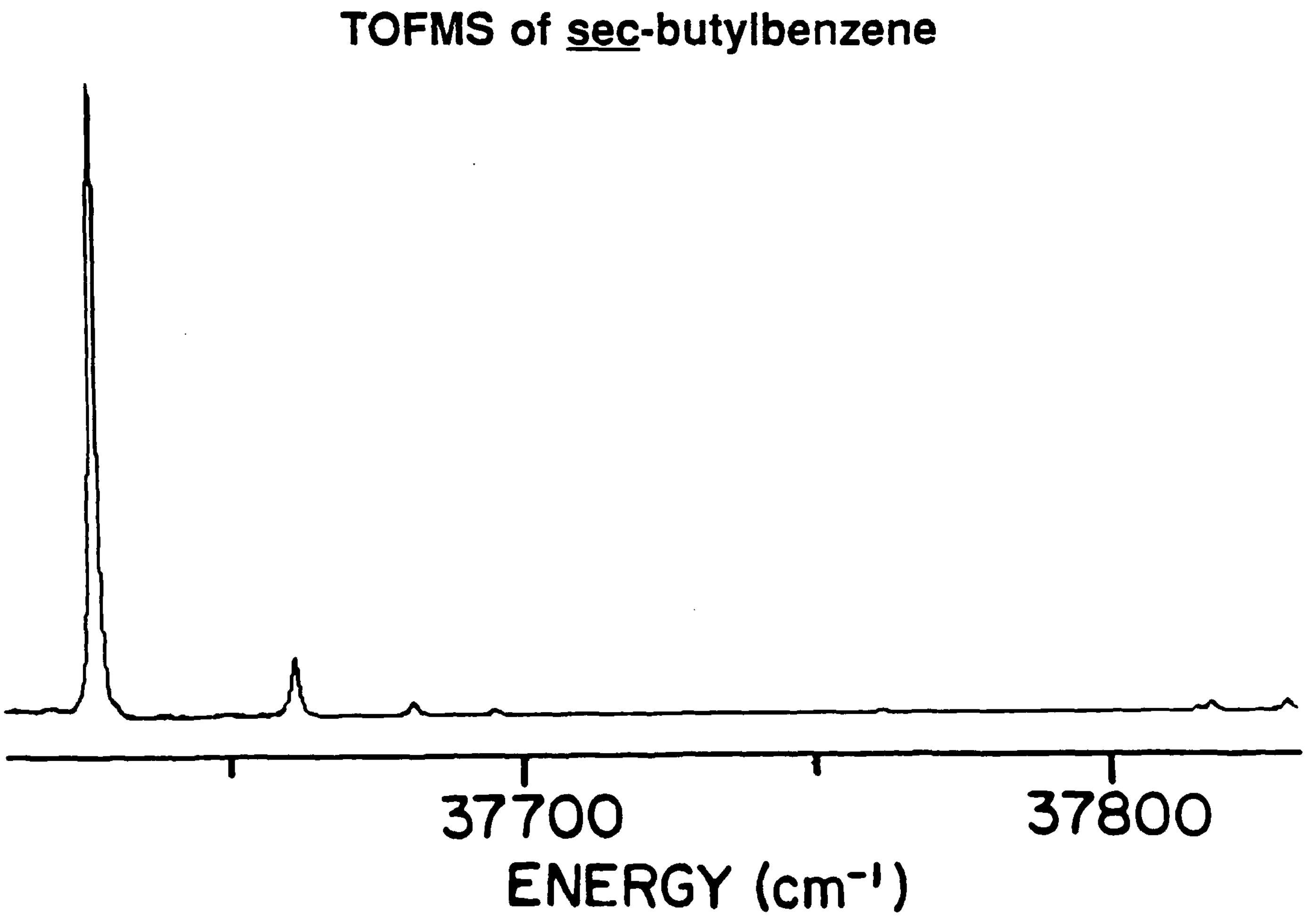
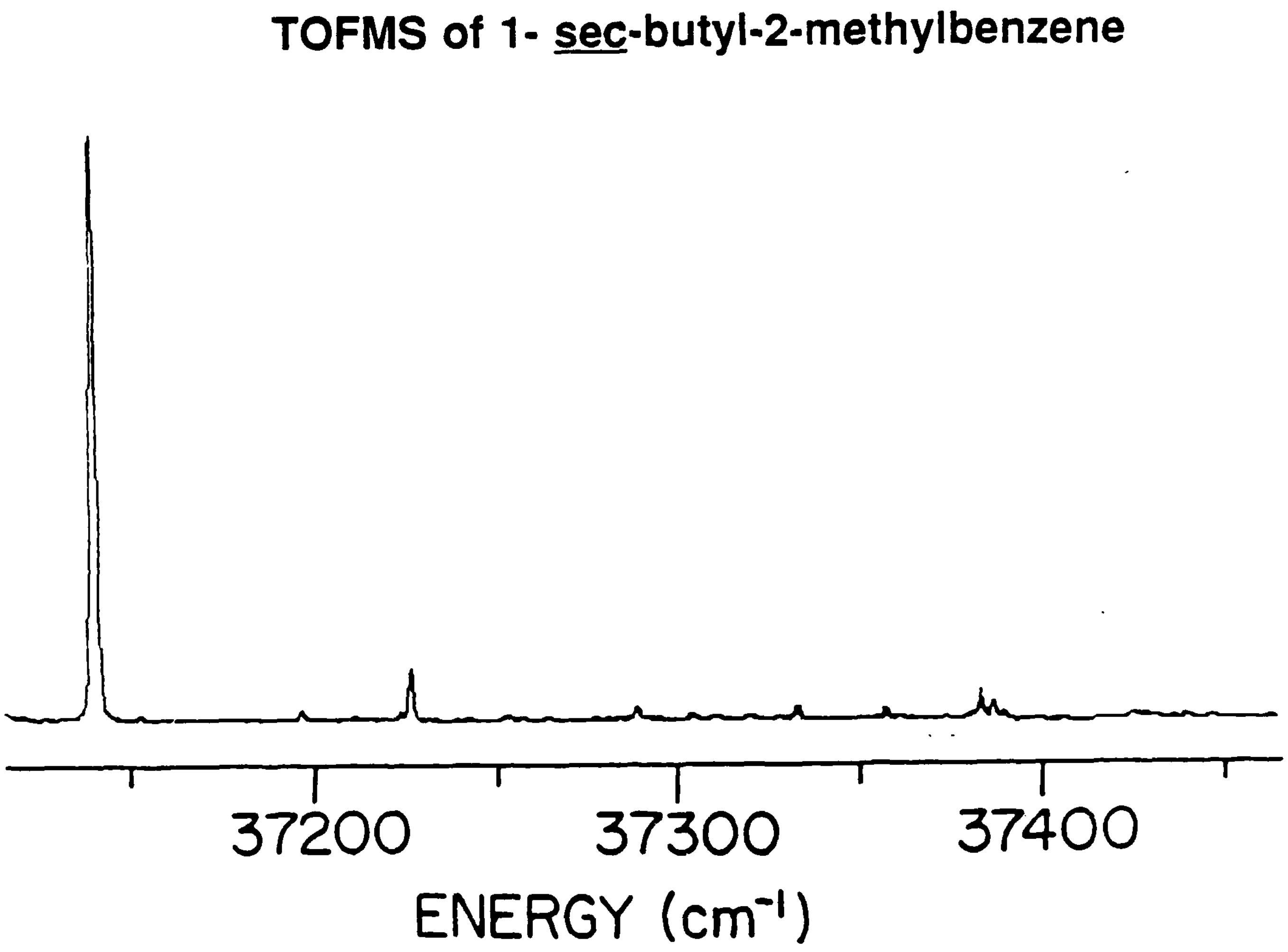

TOFMS of *sec*-butylbenzene

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).


TOFMS of 1- sec-butyl-2-methylbenzene

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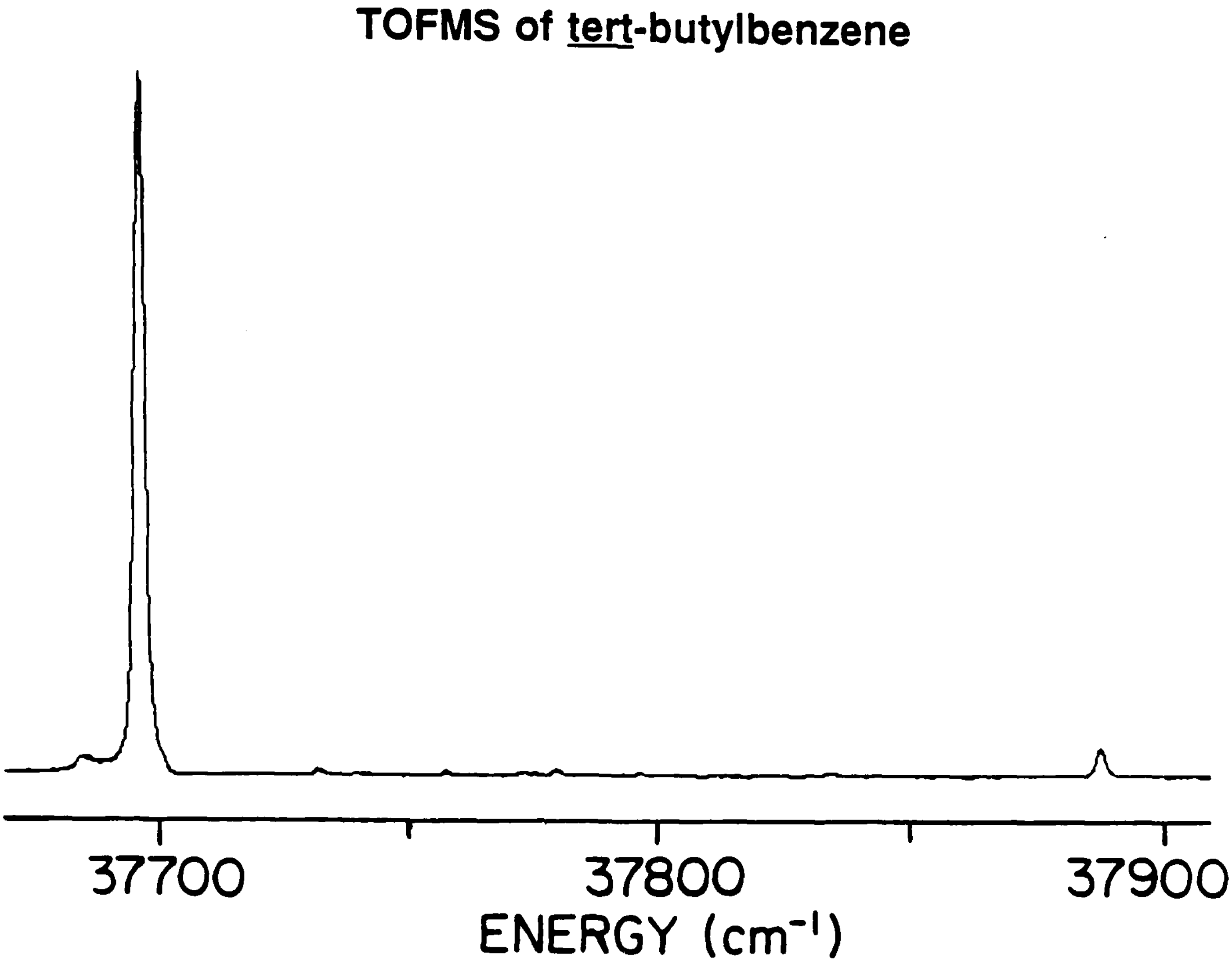

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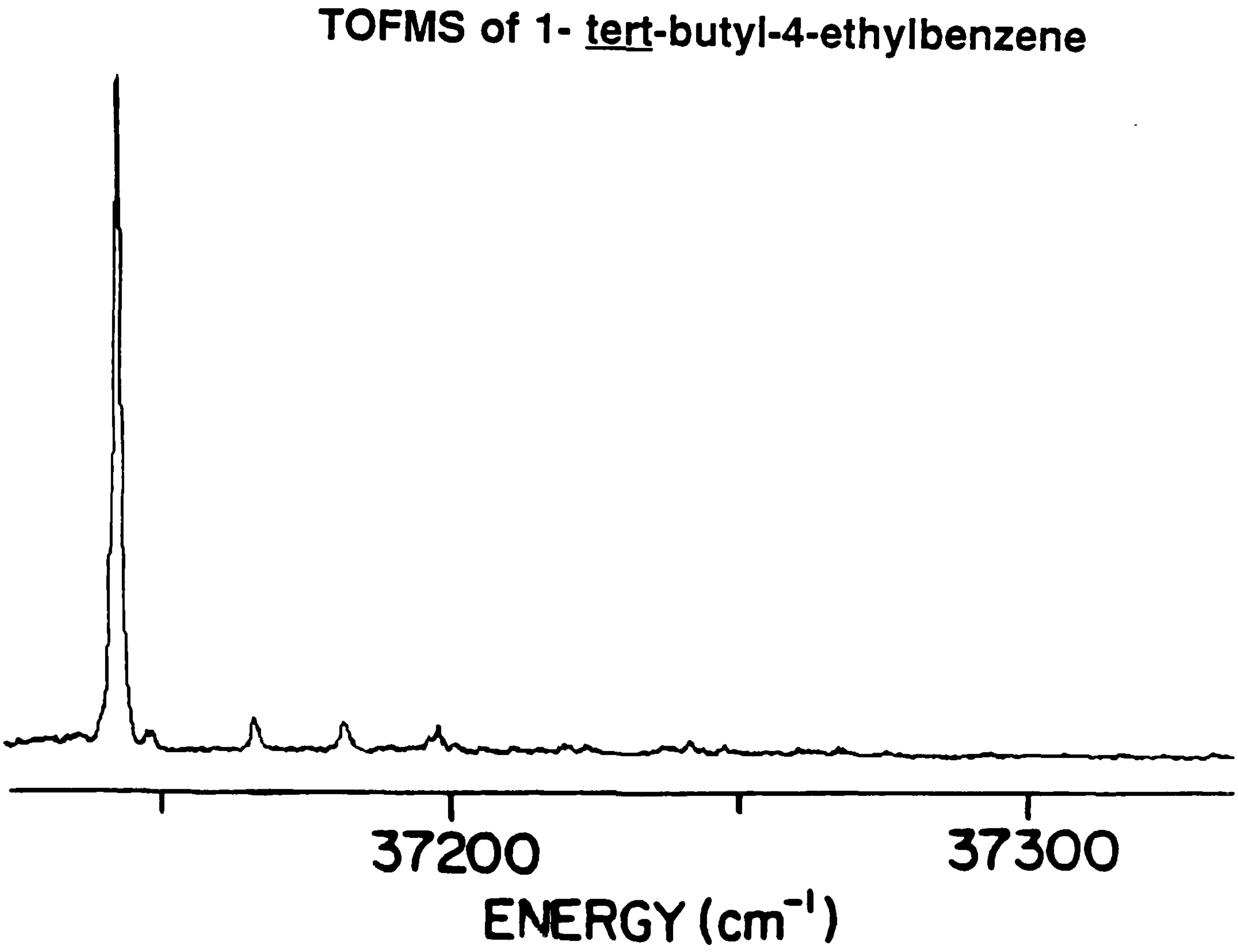

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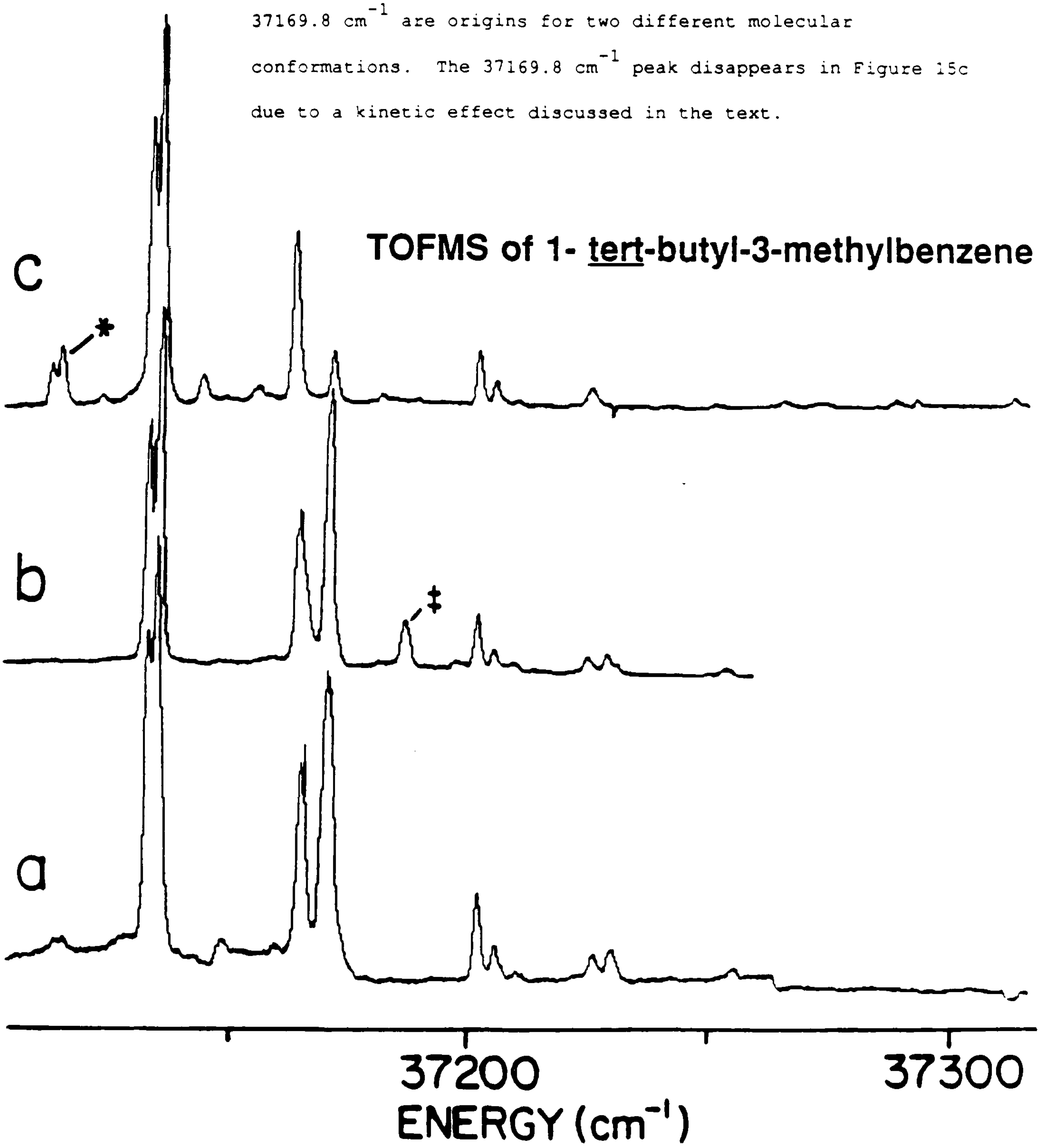

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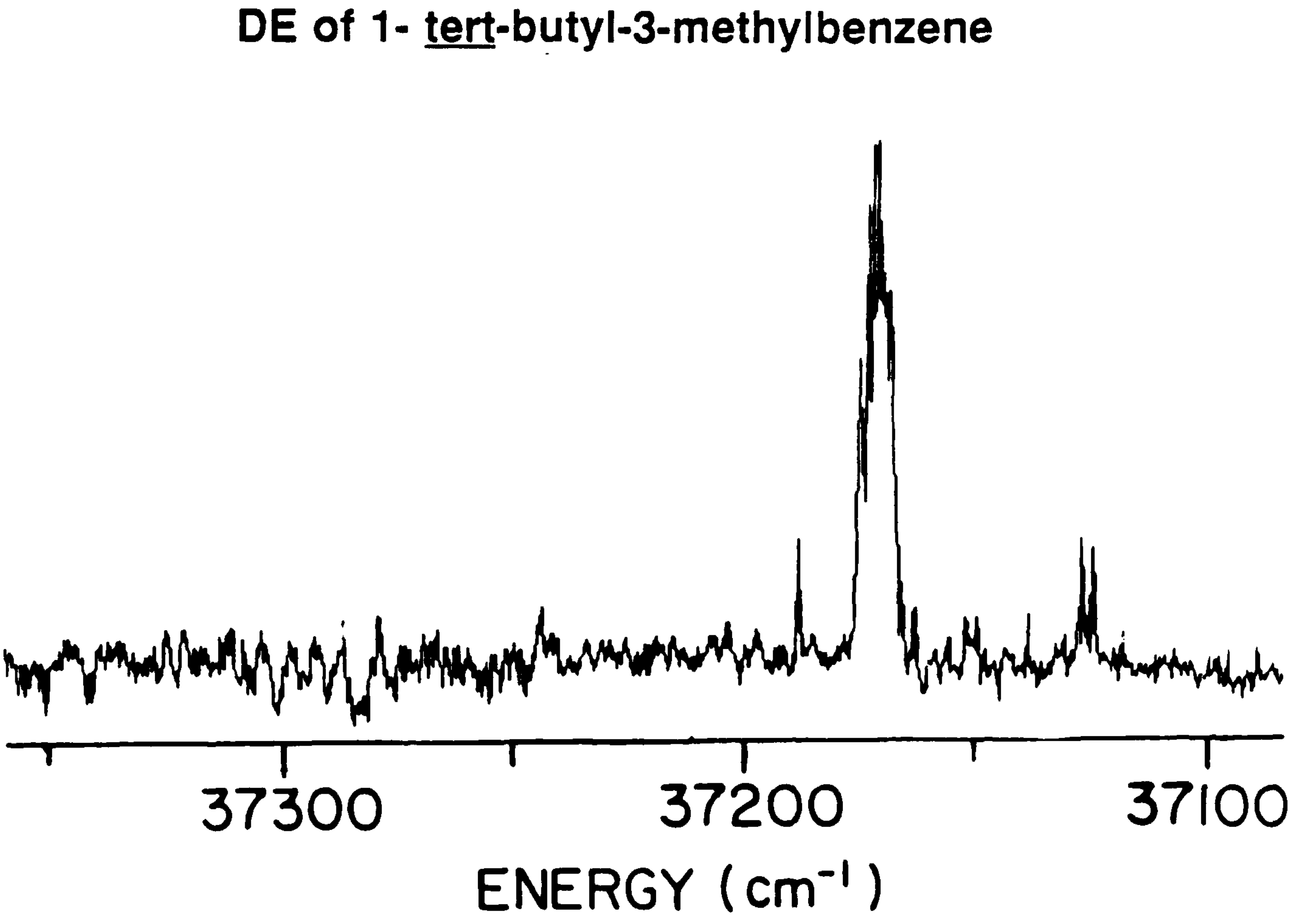

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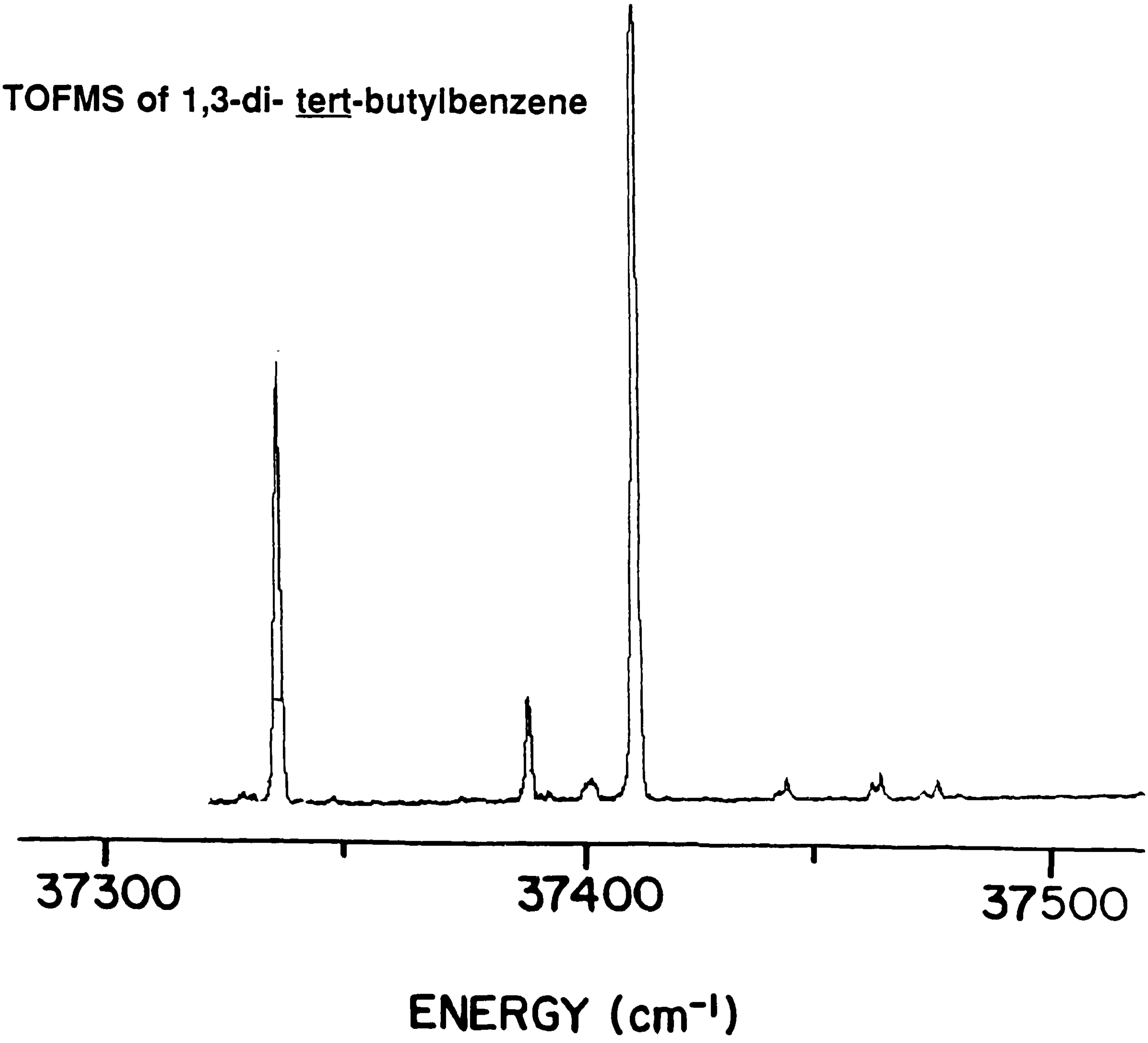

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(1) (a) Philip Morris Research Center. (b) Current address: Baker Performance Chemicals, 3920 Essex Lane, Houston, TX 77027. (c) Colorado State University.

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(10) In pioneering work, Smalley and coworkers have reported[11] the fluorescence excitation (FE) spectra and dispersed fluorescensce 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. One of us (ERB) has previously examined the TOFMS of propylbenzene clusters with methane, ethane, and propane.[12]

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(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 MCMM calculations have estimated a barrier of 2.3 kcal mol^{-1}.[14]

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Author(s): J. I. Seeman, H. V. Secor, P. J. Breen, V. H. Grassian, and E. R. Bernstein

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Supplementary Material

All reactions involving organometallic reagents were carried out under a N_2 atmosphere. Melting points were determined with a Buchi 510 capillary melting point apparatus and are uncorrected. IR spectra were recorded with a Digilab Model FTS-20E. NMR spectra were obtained with either a Varian XL-300 or Varian XL-400 NMR spectrometer, and the chemical shifts are given in ppm downfield from internal Me_4Si. TLC was performed on Analtech/Silica gel GF plates, 250 µm. All chromatography was carried out by using a Harrison Chromatotron® and 4-mm silica gel plates obtained from Analtech, Inc., Newark. DE, or 4-mm plates coated with Kieselgel 60 PF_{254} gipshaltig (EM Reagents). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

1-Ethyl-4-propylbenzene (4).[24] A solution of 4'-propylacetophenone (5.0 g, 30.9 mmol) in methanol (150 mL) containing concd HCl (3 mL) and 10% Pd on charcoal (630 mg) was hydrogenated at 38 psi in a Parr apparatus for 1 h. The catalyst was filtered off and the filtrate neutralized with $NaHCO_3$. The solvent was removed under reduced pressure and the residue taken up with H_2O and CH_2Cl_2. The CH_2Cl_2 phase was separated, dried (Na_2SO_4), concentrated and distilled using a 2" Vigreaux column to give 3.26 g (71%) of 1-ethyl-4-propylbenzene[24] as a colorless oil: bp 28°C (0.03 mmHg); ^1H NMR ($CDCl_3$) δ 0.94 (t, 3H, *J* = 7.3 Hz), 1.21 (t, 3H, *J* = 7.6 Hz), 1.61 (septet, 2H, *J* = 7.5 Hz), 2.52-2.65 (m, 4H), 7.1 (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 13.90, 15.67, 24.68, 28.45, 37.68, 127.68, 128.38, 139.89, 141.42.

(1,2-Dimethylpropyl)benzene (30).[26] A solution of 3-methyl-2-butanone (8.61 g, 0.1 mol) in diethyl ether (100 mL) was treated over a 45 min period at room temperature with phenylmagnesium bromide (34 mL of a 3M soln in ether, 0.1 mol). After being stirred for 45 min, the reaction was quenched with ice. The ether phase was separated, washed sequentially with 5% hydrochloric acid, water, 50% KOH, dried (Na_2SO_4) and concentrated to give 16.0 g of an impure yellow colored oil. Bulb to bulb distillation [up to 80°C (oven) (0.03 mmHg)] gave a forerun which was discarded. 1,2-Dimethyl-1-phenylpropanol[25] (10.25 g, 62.5%) was collected as a colorless oil [81-3°C (oven)(0.03 mmHg)]. A portion of this material (5.0 g) was directly hydrogenated in a Parr shaker in MeOH (150 mL) with 10% Pd on charcoal (500 mg) and concd HCl (2 mL) at 30 psi for 48 h. The catalyst was removed by filtration and the solvent evaporated at reduced pressure. The residue was taken up in hexane, washed with water, 50% KOH and dried (Na_2SO_4). Chromatography followed by vacuum distillation gave 1.5 g (21%) of colorless (1,2-dimethylpropyl)benzene[26]: bp 22°C (0.05 mmHg); ^1H NMR ($CDCl_3$) δ 0.74 (d, 3H, $\underline{J}$ = 6.6Hz), 0.92 (d, 3H, $\underline{J}$ = 6.8 Hz), 1.22 (d, 3H, $\underline{J}$ = 7.0 Hz), 1.75 (heptet, 1H, $\underline{J}$ = 6.8Hz), 2.41 (quintet, 1H, $\underline{J}$ = 7.2 Hz), 7.12-7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.76, 20.18, 21.18, 34.43, 46.86, 125.67, 127.64, 128.01, 147.08.

(1,2,2-Trimethylpropyl)benzene (34).[26] A solution of pivalophenone (4.0 g, 24.7 mmol) in diethyl ether (150 mL) was stirred and cooled to -75°C and treated with methyllithium (30 mL of 1.3M soln, 39 mmol). The reaction was stirred for 15 min and then quenched by the addition of water. The ether phase was washed with water and dried (Na_2SO_4). Evaporation of the solvent followed by bulb to bulb distillation [80°C (oven)(0.04 mmHg)] gave 4.22 g (95%) of 1-phenyl-1,2,2-trimethylpropanol[25] as a colorless oil which was used directly in the next step. A portion of this material (3.72 g, 20.8 mmol) in MeOH (150 mL) along with concd HCl (3 mL) and 10% Pd on charcoal (1 g) was hydrogenated in a Parr apparatus at 30 psi for 4 days and worked up in the same manner as described for **30**. The product was separated from the unreacted starting alcohol by chromatography using hexane as eluant followed by distillation using a 2" Vigreux column to give 1.59 g (47.2%) of (1,2,2-trimethylpropyl)benzene[26] as a colorless oil: bp 22°C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 1.24 (d, 3H, *J* = 7.2 Hz), 2.54 (q, 1H, *J* = 7.2 Hz), 7.13-7.26 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.80, 27.82, 36.65, 49.92, 125.75, 127.41, 129.00, 145.15.

1-Methyl-2-(1-methylpropyl)benzene (28).[27] A solution of ethylmagnesium bromide (12 mL of a 2.85M soln in ether, 34.2 mmol) in diethyl ether (65 mL) was magnetically stirred at room temperature and slowly treated with a solution of 2′-methylacetophenone (3.0 g, 22.35 mmol) in diethyl ether (20 mL) over a period of 1.5 h. After being allowed to stir for an additional 30 min, the reaction was quenched by the addition of ice and 5% HCl. The aqueous phase was separated and extracted with CH_2Cl_2. The combined organic extracts were washed with 50% KOH, dried (Na_2SO_4) and concentrated to give 4.0 g of a pale yellow oil. Residual starting material was removed by dissolving the product in MeOH (10 mL) followed by the addition of a solution of MeOH (40 mL) containing 2,4-dinitrophenylhydrazine (0.8 g) and concd H_2SO_4 (1.6 mL). After being allowed to stand for 6 h, the mixture was filtered and the filtrate neutralized with $NaHCO_3$. Evaporation of the solvent gave an oil which was taken up in hexane, filtered and concentrated to give 2-(2-methylphenyl)-2-butanol (3.13 g) as a pale yellow oil. This material was directly dissolved in MeOH (150 mL) containing 10% Pd on charcoal (400 mg) and concd HCl (1.5 mL) and hydrogenated in a Parr apparatus at 30 psi for 14 h. The solution was filtered and the filtrate concentrated to give a residue which was extracted with hexane. The hexane solution was washed with 50% KOH, dried and concentrated. The residual oil was distilled bulb-to-bulb [30°C (oven)(0.05 mmHg)] to give 1.45 g (43.8%) of colorless 1-methyl-2-(1-methylpropyl)benzene[27]: ^{1}H NMR ($CDCl_3$) δ 0.85(t, 3H, *J* = 7.4 Hz), 1.19 (d, 3H, *J* = 6.9 Hz), 1.53-1.66 (m, 1H), 2.31 (s, 3H), 2.29 (q, 1H, *J* = 6.9H), 7.06-7.18 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.29, 19.59, 21.18, 30.57, 36.17, 125.21, 125.37, 126.12, 130.12, 135.40, 145.82.

1-Methyl-3-(2-methylpropyl)benzene (10). A solution of 3-bromotoluene (8.0 g, 46.7 mmol) in diethyl ether (150 mL) containing Ni(dppp)Cl_2[28] (260 mg, 0.47 mmol) was magnetically stirred and cooled to 0°C and treated with isobutylmagnesium chloride (30.4 mL of a 2M soln in ether, 60.8 mmol) over 20 min. After being allowed to stir for 1 h at 0-10°C, the reaction was stirred at 20-25°C for 48 h, cooled to 0°C and quenched with 5% hydrochloric acid. The ether phase was separated, washed with dilute KOH solution and dried (Na_2SO_4). Evaporation of the ether followed by distillation through a 6" Vigreaux column gave 5.47 g (79%) of 1-methyl-3-(2-methylpropyl)benzene[27]: bp 70°C (12 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.89 (d, 3H, *J* = 6.6 Hz), 1.84 (septet, 1H, *J* = 6.6 Hz), 2.31 (s, 3H), 2.42 (d, 2H, *J* = 7.0 Hz), 6.91-7.18 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.37, 22.39, 30.19, 45.40, 126.11, 126.31, 127.91, 129.88, 137.46, 141.57.

1-Butyl-3-methylbenzene (15).[27] This preparation was carried out in the same manner and scale as described for **10** using 3-bromotoluene, n-butylmagnesium chloride, and a reaction time of 18 h at reflux. Analysis of the reaction product, after workup, showed the presence of 12% residual 3-bromotoluene. The impure product was taken up in ether, cooled to -65°C under a N_2 atmosphere and treated with n-butyllithium (3.5 mL of a 2.5M soln, 8.75 mmol). After warming to room temperature, the reaction was quenched with 5% HCl and worked up as previously described to give 4.5 g (65%) of colorless 1-butyl-3-methylbenzene[27]: bp 80-2°C (12 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.92 (t, 3H, *J* = 7.3Hz), 1.37 (septet, 2H, *J* = 7.3 Hz), 1.51-1.63 (m, 2H), 2.33 (s, 3H), 2.57 (t, 2H, *J* = 7.6Hz), 6.93-7.24 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 13.99, 21.40, 22.48, 33.79, 35.67, 125.44, 126.32, 128.14, 129.25, 137.68, 142.83.

1-Methyl-2-(2-methylpropyl)benzene (11).[29] This preparation was carried out on the same scale exactly as described for **10** using isobutylmagnesium chloride and 2-bromotoluene and yielded 5.04 g (72.8%) of 1-methyl-2-(2-methylpropyl)benzene[29] as a clear colorless oil: bp 74-5°C (12 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.92 (d, 3H, *J* = 6.6 Hz), 1.85 (septet, 1H, *J* = 6.7 Hz), 2.30 (s, 3H), 2.47 (d, 2H, *J* = 7.1 Hz), 7.07-7.12 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 19.49, 22.59, 29.16, 42.61, 125.55, 125.77, 129.92, 130.13, 136.03, 139.87.

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