dialkyl), increasing alkylation increases the PA's. (2) For disilyl ethers, replacement of a silicon by carbon increases the PA by 3–6 kcal mol^{-1}. (3) For alkyl silyl ethers, replacement of the silicon by carbon leads to variable effects on the PA. For isomers H_3COSiR_3 and H_3SiOCR_3, the methyl ethers have the higher PA's. (4) For methyl ethers, CH_3OY, PA's decrease along the series Y = $(CH_3)_3C \approx (CH_3)_3Si > CH_3SiH_2 > CH_3CH_2 > CH_3 \approx SiH_3$. This substituent order is consistent with the gas-phase observations of Pitt et al., namely, $(CH_3)_3C \geq (CH_3)_2CH \geq (CH_3)_3Si \geq (CH_3)_2SiH \geq CH_3CH_2 > CH_3 > H$.[6] The most surprising result here is the general similarity between the gas-phase proton affinities for alkyl silyl ethers and analogous dialkyl ethers.

A final observation may be made regarding the computed entropy terms. Both disiloxane and dimethyl ether possess comparatively more positive entropy changes upon protonation. These results partially from the fact that both molecules possess C_{2v} symmetry and, upon protonation, experience less rotational entropy loss than their lower symmetry counterparts, equivalent to R ln 2 or ca. 0.4 kcal mol^{-1}.[34] Inspection of the individual entropy contributions confirms that both methyl ether and disiloxane have lower rotational entropies. However, the bulk of the entropy loss is accounted for by the change in translational entropy upon protonation.

Conclusion

The results presented in this paper document the geometrical and energetic changes that occur for the gas-phase protonation reactions of a series of alkyl and silyl ethers. The general trend among the alkyl ethers upon protonation is toward lengthening of the O–CR$_3$ and O–CH$_3$ bonds by roughly 0.14 and 0.08 Å, respectively, and widening the C–O–C angle by ca. 5°. The silyl ethers display similar trends, with more pronounced O–SiR$_3$ bond lengthening of 0.170–0.20 Å and Si–O–C angle widening of ca. 2°.

Correlation energy corrections and vibrational energy terms are needed for the reliable computation of absolute gas-phase proton affinities and basicities. The accord with the available experimental data suggest that the predicted thermodynamic results are within 3 kcal mol^{-1} of the true values. The low gas-phase basicity of disiloxanes has been confirmed, while the similar gas-phase basicity for dialkyl ethers and analogous alkyl silyl ethers has also been quantified.

Acknowledgment. Gratitude is expressed to the National Science Foundation for support of this work and to Scott G. Wierschke for computational assistance.

Supplementary Material Available: Detailed results of the 6-31G(d) geometry optimizations for the molecules in Figures 1–5 in Gaussian archive formate (6 pages). Ordering information is given on any current masthead page.

---

(34) Bailey, W. F.; Monahan, A. S. *J. Chem. Educ.* 1978, 55, 489.

Supersonic Jet Studies of Ethoxybenzenes: Geometry of Their Minimum Energy Conformations

E. R. Bernstein,* Hoong-Sun Im, and Mark A. Young[†]

Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523

Henry V. Secor, Ronald L. Bassfield, and Jeffrey I. Seeman*

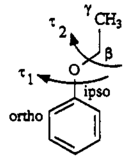
Phillip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261

Received February 13, 1991

Supersonic jet mass resolved excitation spectroscopy and MOPAC 5/AM1 calculations are employed to demonstrate that the minimum energy conformation of ethoxybenzene and a number of its ortho-unsubstituted (i.e., sterically unhindered) derivatives is the planar form for which $\tau_1(C_{ortho}–C_{ipso}–O–C_\beta) = 0°$ and $\tau_2(C_{ipso}–O–C_\beta–C_\gamma) = 180°$. For 1-ethoxy-3-methylbenzene, two spectroscopic origin transitions are observed, one each for the conformations in which the $C_\beta H_2–C_\gamma H_3$ fragment is syn and anti to the C(3)-methyl substituent. For 1-ethoxy-4-ethylbenzene, a single origin transition is observed, as demonstrated by examination of two deuteriated derivatives.

Introduction

Aromatic compounds possessing alkyl or heteroalkyl substituents are ubiquitous in nature and play an important role in organic chemistry as a whole. Conformational analysis of these substances continues to receive intense attention,[1] in part because the literature frequently contains conflicting conclusions regarding the geometry of the minimum energy conformations of specific substituents.[2] A case in point is the aromatic ethoxy substituent, for which ethoxybenzene (phenetole, 1) is the prototype. On



1

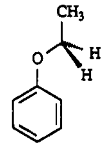
$$\tau_1 = \tau(C_{ortho}–C_{ipso}–O–C_\beta)$$
$$\tau_2 = \tau(C_{ipso}–O–C_\beta–C_\gamma)$$

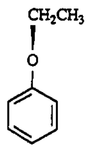
the basis of room-temperature IR data, the all (heavy

[†] Present address: Department of Chemistry, University of Iowa, Iowa City, IA 52242.

0022-3263/91/1956-6059$02.50/0

atom) planar 2 conformation was suggested for 1,[8] while both a planar and an orthogonal (minor) contributor 3 were indicated by IR, UV, and ^{13}C NMR spectral data.[9] Somewhat contradictory conclusions were reached by two photoelectron spectroscopic studies, one implying a single planar conformation for 1[10] while another indicating the presence of a minor (16%) perpendicular component.[11] Perpendicular conformations have been used as "standard geometries" for various theoretical studies.[12]


2

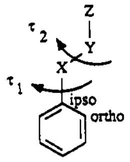

3

A great deal of work, of both an experimental and theoretical nature, has been devoted to elucidating the structure of methoxybenzene and various substituted methoxybenzenes.[7] In methoxybenzene itself, the preferred conformation of the methoxy group is found to be planar with respect to the aromatic ring.[7] The stabilization resulting from conjugation between lone pair electrons in the p-type oxygen orbital and the π system of the aromatic ring dominates over repulsive steric forces. The substituted methoxybenzenes are also planar except in cases for which overriding steric factors, such as found in ortho-substituted molecules, force the methoxy group out of the plane.[7c,d]

The stability conferred by a planar conformation in the methoxybenzenes does not hold true for isosteric aromatics, e.g., ethylbenzene and benzyl alcohol. The ethyl group in ethylbenzene is predicted theoretically,[3c] and confirmed experimentally,[3a,b] to lie perpendicular to the plane of the ring, i.e., $\tau(C_{ortho}–C_{ipso}–C_\alpha–C_\beta) = 90°$. A combination of steric repulsion and hyperconjugation between the C–C σ bond of the substituent and the aromatic π system makes the perpendicular configuration the most favorable. Similar considerations apply to the hydroxymethyl group in benzyl alcohol, which has been recently found to lie perpendicular to the plane of the ring, i.e., $\tau(C_{ortho}–C_{ipso}–C_\alpha–O) = 90°$.[5b,c]

Supersonic molecular jet laser spectroscopy has recently been employed for conformational analysis of substituted aromatic systems.[3b,4,5b,6c,7b,13-15] As shown in Table I, the geometries of the minimum energy conformation(s) of a wide variety of substituents have been assigned. Further, in some cases, spectroscopic signals are observed for two or more stable conformations of a single compound. The key features of laser jet spectroscopy that render the technique particularly useful for conformational analysis have been detailed previously:[5c] the expansion results in molecules at near 0 K; the molecules are isolated; one origin (0^0_0) transition is observed for each individual stable conformation and the converse;[16] and the resolution of the

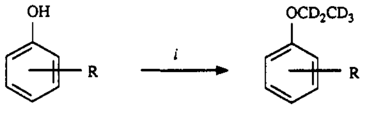
Table I. Conformations of Substituted Benzenes as Established by Laser Jet Spectroscopy



	$\tau_1 = \tau(C_{ortho}–C_{ipso}–X–Y)$ (deg)	$\tau_2 = \tau(C_{ipso}–X–Y–Z)$ (deg)	ref
ethylbenzene	90		*a*
propylbenzene	90	60/180	*b*
methoxybenzene	0		*c*
styrene	0		*d*
α-methylstyrene	30		*e*
allylbenzene	90		*f*
benzyl alcohol	90		*g*
benzyl fluoride	90		*g*
ethoxybenzene	0	180	this work

[a] Reference 3b. [b] Reference 4. [c] Reference 7b. [d] Reference 13. [e] Reference 14. [f] Breen, P. J.; Bernstein, E. R.; Seeman, J. I.; Secor, H. V. *J. Phys. Chem.* 1989, *93*, 6731. [g] Reference 5b,c.

Scheme I[a]



4, R = H
5, R = 3-CH_3
7, R = 4-CD_3CD_2

[a] Key: i, n-Bu_4NOH, KOH, H_2O/CD_3CD_2Br, CH_2Cl_2.

---

(1) For leading references, see: (a) Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: Deerfield Beach, FL, 1985. (b) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* 1985, *18*, 80. (c) Berg, U.; Sandström, J. *Adv. Phys. Org. Chem.* 1989, *25*, 1. (d) Pross, A.; Random, L. *Adv. Phy. Org. Chem.* 1981, *13*, 1. (e) *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I., Hargittai, M., Eds.; VCH Publishers: Deerfield Beach, FL, 1988. (f) Parr, W. J. E.; Schaefer, T. *Acc. Chem. Res.* 1980, *13*, 400.

(2) For example, recent publications from numerous labortories have focused attention on the conformational properties of ethylbenzenes,[3] propylbenzenes,[4] benzyl alcohols,[5] benzyl fluorides,[5c,6] and methoxybenzenes.[7] Leading references are cited in these references.

(3) (a) True, N. S.; Farag, M. S.; Bohn, R. K.; MacGregor, M. A.; Radhakrishan, J. *J. Phys. Chem.* 1983, *87*, 4622. (b) Breen, P. J.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* 1987, *87*, 3629. (c) Kao, J. *J. Am. Chem. Soc.* 1987, *109*, 3817 and references cited therein.

(4) (a) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* 1987, *87*, 1927. (b) Song, X.; Pauls, S.; Lucia, J.; Du, P.; Davidson, E. R.; Reilly, J. P. *J. Am. Chem. Soc.* 1991, *113*, 3202.

(5) (a) Schaefer, T.; Sebastian, R.; Peeling, J.; Penner, G. H.; Hoh, K. *Can. J. Chem.* 1989, *67*, 1015. (b) Seeman, J. I.; Secor, H. V.; Im, H.-S.; Bernstein, E. R. *J. Chem. Soc., Chem. Commun.* 1990, 87. (c) Im, H.-S.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* 1991, *113*, 4422.

(6) (a) Brownlee, R. T. C.; Craik, D. J. *Tetrahedron Lett.* 1980, *21*, 1681. (b) Schaefer, T.; Beaulieu, C.; Sebastian, R.; Penner, G. H. *Can. J. Chem.* 1990, *68*, 581.

(7) (a) Schaefer, T.; Sebastian, R. *Can. J. Chem.* 1989, *67*, 1027. (b) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* 1989, *111*, 1958. (c) Konschin, H. THEOCHEM, 1988, *168*, 293. (d) Schaefer, T.; Sebastian, R.; Lemire, A.; Penner, G. H. *Can. J. Chem.* 1990, *68*, 1393.

(8) Katritzky, A. R.; Pinzelli, R. F.; Topsom, R. D. *Tetrahedron* 1972, *28*, 3441.

(9) Panov, A. M.; Ratovskii, G. V.; Kalabin, G. A. *Zh. Obshch. Khim.* 1983, *53*, 1669; *Chem. Abstr.* 1983, *99*, 211819f.

(10) Dewar, P. S.; Ernstbrunner, E.; Gilmore, J. R.; Godfrey, M.; Mellor, J. M. *Tetrahedron* 1974, *30*, 2455.

(11) Friege, H.; Klessinger, M. *Chem. Ber.* 1979, *112*, 1614.

(12) See, for example: (a) Eberhardt, M. K.; Chuchani, G. *J. Org. Chem.* 1972, *37*, 3654. (b) Testa, B.; Mihailova, D. *J. Med. Chem.* 1978, *21*, 683.

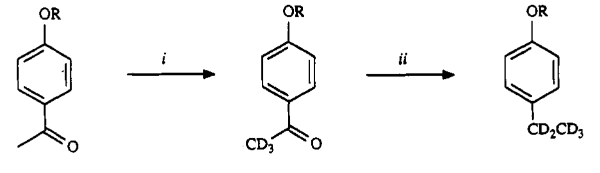
(13) Grassian, V. H.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Phys. Chem.* 1989, *93*, 3470.

(14) Grassian, V. H.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Phys. Chem.* 1990, *94*, 6693.

(15) (a) Okyugama, K.; Mikami, N.; Ito, M. *J. Phys. Chem.* 1985, *89*, 5617. (b) Rizzo, T. R.; Park, Y. D.; Peteanu, L. A.; Levy, D. H. *J. Chem. Phys.* 1986, *84*, 2534. (c) Howells, B. D.; Martinez, M. T.; Palmer, T. F. Simons, J. P.; Walters, A. *J. Chem. Soc., Faraday Trans.* 1990, *86*, 1949. (d) Sipior, J.; Sulkes, M.; Auerbach, R.; Boivineau, M. *J. Phys. Chem.* 1987, *91*, 2016.

(16) Observation of a single origin transition in this work implies that either (a) only a single stable ground-state conformation exists, (b) one conformation is significantly more stable than the others under the conditions of the expansion, or (c) less likely, but possible, the transition energies for two origin transitions are unresolved.

Scheme II[a]



8a, R = H
8b, R = CH_3CH_2

9a, R = H
9b, R = CH_3CH_2

10, R = H
6, R = CH_3CH_2

[a] Key: i, NaOD, D_2O; ii, D_2, Pd/C.

experiment is excellent (<1 cm^{-1}; 350 cm^{-1} = 1 kcal/mol).

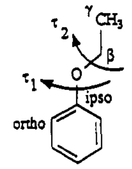
For different conformations of a molecule, the difference in the $\{S_0–S_1\}$ energy can be on the order of a few to hundreds of wavenumbers. Hence 0_0^0 transitions are easily observed for individual components of a mixture or for individual conformations of a single compound. Since each distinct conformation will typically have an intense associated origin transition, conformational analysis is accomplished by first assigning and then counting the number of origin transitions for particular asymmetrically substituted molecules. Other substituents, with known conformations in aromatic systems, can be used to differentiate between various molecular orientations that would otherwise be energetically degenerate. In the absence of steric effects, e.g., buttressing, alkyl substituents will generally not perturb the system, or in turn, be perturbed by the system, so that their known conformation can be assumed to be preserved.

Experimental Section

Mass-resolved excitation spectra (MRES, also referred to as time of flight mass spectra),[17] are obtained as described in detail previously.[18] All spectra are recorded through a one-color, two-photon ionization process. Care is taken to obtain the true relative intensities of spectral features by attenuating the probe laser with neutral density filters and reducing the total ion signal level. A pulsed valve, operating at 10 Hz, with a 800-μm orifice is utilized to generate the supersonic expansion. Backing pressures of the helium expansion gas are typically on the order of 100 psig. The higher expansion pressures are necessary due to the difficulty in cooling the ethoxybenzenes. The liquid samples are held in a reservoir at room temperature. All samples, except for the deuteriated substances, were purchased commercially. The deuteriated compounds 4–7 were prepared as outlined in Schemes I and II. Full details of the synthesis of 4–7 and the ^1H and ^{13}C NMR spectra of these compounds are found in the supplementary material.

Results and Discussion

Table II. Definition of Conformations for Ethoxybenzenes



	$\tau_1 = \tau(C_{ortho}–C_{ipso}–O–C_\beta)$ (deg)	$\tau_2 = \tau(C_{ipso}–O–C_\beta–C_\gamma)$ (deg)
planar-syn	0	0
planar-anti (2)	0	180
planar-gauche	0	$0 > \tau_2 > 180$
perpendicular (3)	90	any value
gauche	$0 > \tau_1 > 90$	any value

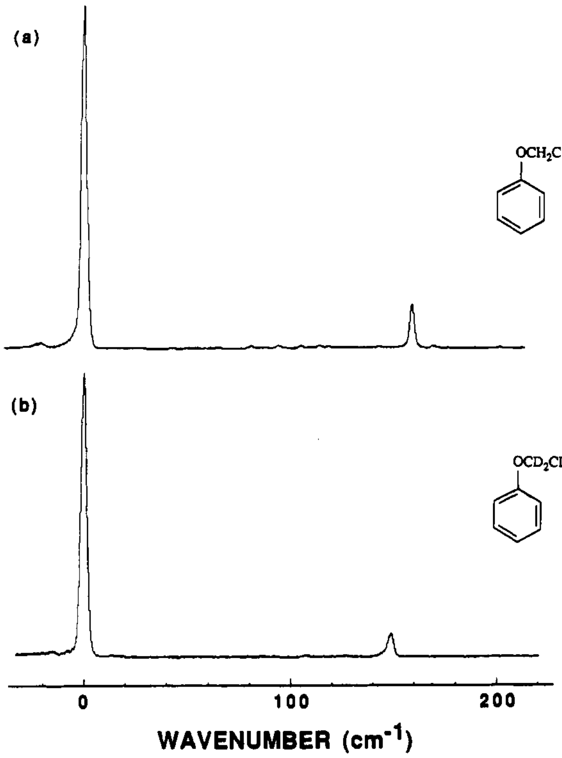


Figure 1. (a) The MRES of ethoxybenzene (1). The origin transition is at 36 372 cm^{-1}. The feature 166 cm^{-1} to higher energy is an ethoxy vibrational mode. (b) The MRES of (ethoxy-d_5)-benzene (4). The origin transition lies at 36 365 cm^{-1}, and the ethoxy-d_5 chain mode is found 156.5 cm^{-1} to higher energy.

As shown in 1, two torsion angles, $\tau_1 = \tau(C_{ortho}–C_{ipso}–O–C_\beta)$ and $\tau_2 = \tau(C_{ipso}–O–C_\beta–C_\gamma)$ characterize the conformation of the ethyl phenyl ether substructure. Table II classifies a simplified set of five conformational types for this system. Note that in Table II, τ_2 is not specified for both the perpendicular and gauche conformations because, as demonstrated subsequently, neither of these conformational types is found to be present in this work and thus further classification is unnecessary.

A. Ethoxybenzene (Phenetole, 1). A 200 cm^{-1} section of the mass resolved excitation spectrum (MRES) of 1 is shown in Figure 1a. The spectrum is distinguished by a strong feature at 36 372 cm^{-1} and another, much weaker, peak located 166 cm^{-1} to higher energy. We interpret the strong feature in the spectrum as arising from the 0_0^0 transition ($S_1 \leftarrow S_0$) of the molecule and the weaker feature as being due to a vibronic transition involving a low-frequency mode, presumably a motion involving the ethoxy group.[16]

Such an explanation is verified by observing the MRES of the deuteriated analogue 4, as depicted in Figure 1b. The overall appearance of the spectrum is similar to that of ethoxybenzene except that the smaller feature is now located 156.5 cm^{-1} from the main peak, a shift of 5.8% upon deuteriation. For a pure ethoxy motion, the increased mass upon deuteriation would result in a frequency that is 5.1% lower, quite close to the observed decrease. Thus, the small feature is almost certainly a vibronic transition and only one origin is found for ethoxybenzene.

---

[17] The name "one (and two) color mass resolved excitation spectroscopy" is 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 ($S_1 \leftarrow S_0$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($I^+ \leftarrow S_1$). 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 $S_1 \leftarrow S_0$ "absorption" or excitation spectrum of a mass selected species is obtained. This technique has also been referred to as time of flight mass spectroscopy.[4a]

[18] Bernstein, E. R.; Law, K.; Schauer, M. *J. Chem. Phys.* **1984**, *80*, 207.

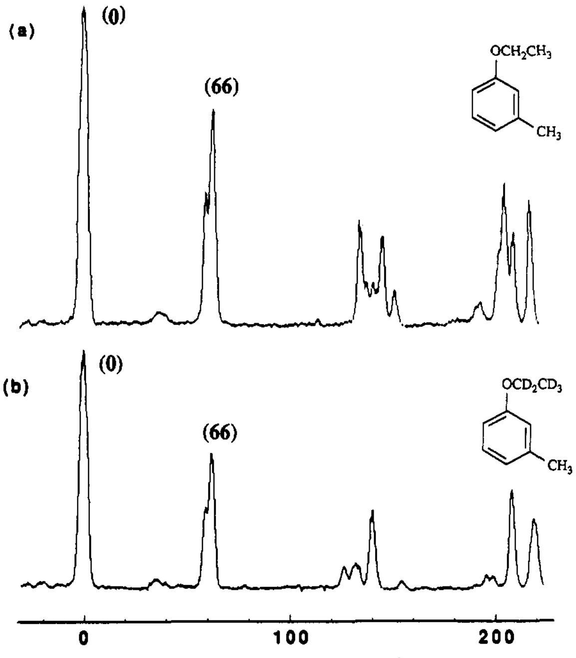
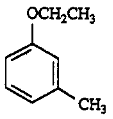


Figure 2. (a) The MRES of 1-ethoxy-3-methylbenzene (11). Two origins are found at 36 037 and ~36 100 cm^{-1}. (b) The MRES of 1-(ethoxy-d_5)-3-methylbenzene (5) has origin transitions at approximately the same positions.

This observation is consistent with ethoxybenzene existing in a single stable conformation,[16] although the orientation of the ethoxy with respect to the ring cannot be discerned from these data alone.

Table III (found in the supplementary material) lists the results of a two-dimensional potential energy contour AM1 calculation of 1 about the τ_1 and τ_2 coordinates. The global energy minimum is found at $\{\tau_1 = 0°, \tau_2 = 180°\}$, i.e., the planar-anti conformation 2. A number of local minima are found on the energy surface, with the next most stable (+1.3 kcal) being a planar-gauche form at $\{\tau_1 = 0°, \tau_2 = 75°\}$. The MRES of 1 and 4 and the calculations are most consistent with the planar-anti conformation 2 as the single conformation for this molecule.

B. 1-Ethoxy-3-methylbenzene (11). A portion of the MRES of 1-ethoxy-3-methylbenzene is presented in Figure 2a. The spectrum is much richer than that found for ethoxybenzene. The MRES shown in Figure 2a is characterized by a strong feature at 36 037 cm^{-1}, which is the lowest energy transition located. The peak has a spectral bandwidth of 5.6 cm^{-1} that is greater than the 0.4 cm^{-1} bandwidth of our laser and substantially broader than other spectral features that are isolated and not part of multiplets. Attempts at increased cooling of the sample did not affect the width of the line, discounting any contribution to the line width from an elevated rotational temperature. Another intense band is located at 36 103 cm^{-1} and has an obvious doublet character. A series of relatively strong features is located at still higher energies.



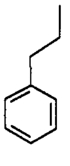
11

The spectrum of 11 does not easily lend itself to a straightforward analysis, but considerable insight can be gained by examining the deuterated compound, 1-(ethoxy-d_5)-3-methylbenzene (5). This spectrum is shown in Figure 2b. The two prominent features (36 037 and 36 103 cm^{-1}) at the low-energy end of the spectrum remain essentially unchanged in position, while considerable differences from the MRES of the nondeuteriated substrate are clear among the higher energy bands.

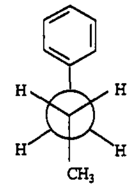
A consistent analysis of the data can be constructed if the first two main features in the spectra are considered to be origin due to two different molecular conformations present in the molecular beam. These two bands do not move relative to one another upon deuteration and shift only slightly in absolute energies. The width of the 36 037 cm^{-1} feature and the doublet structure of the 36 103 cm^{-1} feature are most likely due to the splitting between the $0a_1$–$0a_1$ and 1e–1e transitions of the methyl group rotor levels.[19] Since the deuterated methyl compound 1-ethoxy-3-(methyl-d_3)benzene is not examined, the identification of the higher energy peak at 36 103 cm^{-1} as a methyl rotor transition cannot be immediately ruled out. However, on the basis of the MRES of 1-methoxy-3-methylbenzene,[7b] the first intense methyl rotor transition in 1-ethoxy-3-methylbenzene should be in excess of 140 cm^{-1} to higher energy of the origin.

The majority of the remaining features in the spectrum are most likely due to motions involving the ethoxy group. The two features at 36 249 cm^{-1} and 36 261 cm^{-1} do not shift upon deuteration and are probably due to methyl rotor transitions. They are most likely too high in energy to be origin transitions involving other conformations since only relatively small (<100 cm^{-1}) energy differences between different molecular conformations are expected.

The presence of two origin transitions and hence two different conformations for 1-ethoxy-3-methylbenzene indicates that at least some portion of the ethoxy substituent is asymmetric relative to the C_1–C_4 axis. This is strong evidence *against* the perpendicular-anti conformation 3 where $\tau_2 = 180°$. This is in contrast with the situation found for the isosteric propylbenzene (12), in which the most stable conformer is **12a**.

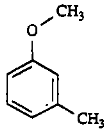


12

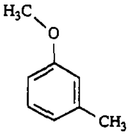


12a

The closest analogous system to 1-ethoxy-3-methylbenzene (11) that has been examined to date is 1-methoxy-3-methylbenzene (13) for which origins are observed at 36 047.5 and at 36 113.8 cm^{-1}.[7b] These origins are assigned to the planar-syn **13s** and planar-anti **13a** conformations.[7b] The two origins for 11 are separated by the same energy as the two origins found for 13. This spectral similarity strongly suggests a structural similarity; that is, a planar-anti conformation 2 for ethoxybenzenes as suggested previously from both experiments and calculations.



13s



13a

---

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

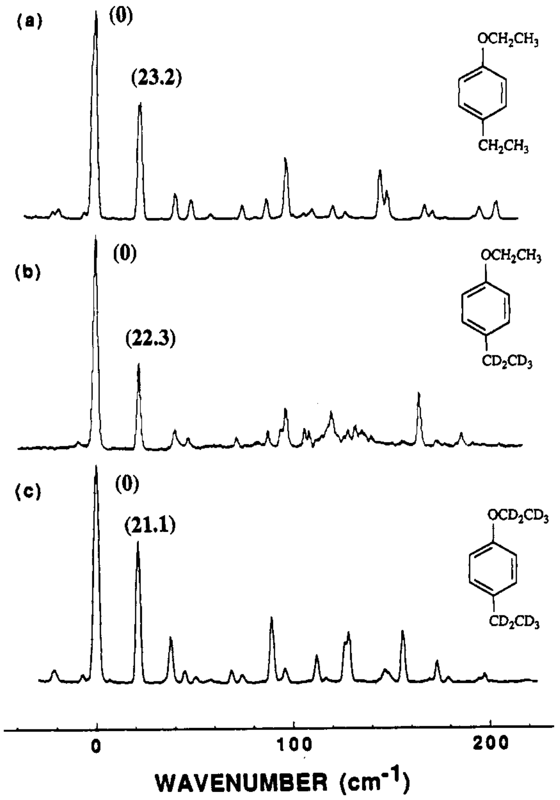
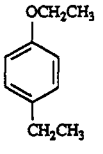


Figure 3. (a) The MRES of 1-ethoxy-4-ethylbenzene (14). The origin transition (35 562 cm^{-1}) is indicated at 0 cm^{-1} on this scale. (b) The MRES of 1-ethoxy-4-(ethyl-d_5)benzene (6). The origin is found at 35 563 cm^{-1}. (c) The MRES of 1-(ethoxy-d_5)-4-(ethyl-d_5)benzene (7). The origin transition is found at 35 500 cm^{-1}. The common features in the latter two spectra (Figures 3b and 3c) at ca. 22 cm^{-1} have ~5 and 10% isotopic shifts, respectively, relative to the same features shown in Figure 3a. The features at ca. 22 cm^{-1} are thus not origin transitions and are assigned to be low-frequency vibrational modes of their respective molecules.

C. 1-Ethoxy-4-ethylbenzene (14). The spectrum of 1-ethoxy-4-ethylbenzene is shown in Figure 3a. A strong feature at 35 562.2 cm^{-1} is most prominent. A closely spaced peak located at 35 585.5 cm^{-1} ($\Delta\upsilon$ = 23.2 cm^{-1}) is approximately 30% of the intensity of the main peak. A number of relatively weaker bands are observed at higher energies. The spectra of the d_5 and d_{10} analogues 6 and 7 are shown in Figure 3b and c, respectively. The three spectra are very similar.



14

The aromatic ethyl group has previously been shown to lie perpendicular to the plane defined by the aromatic ring.[3] The data for 1-ethoxy-3-methylbenzene presented in the previous text indicate that at least part of the ethoxy group is located in the plane. If the entire ethoxy substituent chain were in the plane of the aromatic ring, one origin transition would be expected to manifest itself for the MRES spectrum of 14. A conformation with the methyl group of the ethoxy ligand perpendicular to the plane would result in two origins, corresponding to syn and anti conformations with respect to the 4-ethyl group.

The MRES of 1-ethoxy-4-(ethyl-d_5)benzene (6; see Figure 3b) indicates that the smaller, higher energy feature in the spectrum shifts ~4% to lower energy after deuteriation of the 4-ethyl substituent. A pure ethyl motion would lead to an anticipated shift of 8.2%, approximately twice as large as the shift actually observed. A 4% shift would not be surprising if such a low-frequency motion involved a more complicated normal coordinate. In fact, a motion involving both the ethyl and the ethoxy groups would evince a frequency shift of 3.3% upon deuteriation of the 4-ethyl substituent, quite close to the measured value. The higher energy feature would then appear to be due to a vibronic transition, and thus, only a single origin would be represented in the spectrum.

In order to establish that only a single 0_0^0 transition is present in the MRES of 1-ethoxy-4-ethylbenzene, the MRES of 1-(ethoxy-d_5)-4-(ethyl-d_5)benzene (7) was obtained. The MRES of 7, shown in Figure 3c, indicates that the first strong feature to the blue (to higher energy) of the origin occurs at +21.1 cm^{-1}. This represents an 8.3% isotope shift to lower energy for this transition, compared to that of the totally protiated species 14 (Figure 3a), a shift clearly indicative of a vibronic transition. Hence, only a single 0_0^0 transition is obtained obtain for these 1-ethoxy-4-ethylbenzenes. *The accumulated experimental data obtained from 6, 7, and 14 indicate that all three of the heavy atoms in the ethoxy group lie in the plane of the aromatic ring.*

Conclusions

In summary, the MRES of ethoxybenzene and 1-ethoxy-4-ethylbenzene show one origin transition while the MRES of 1-ethoxy-3-methylbenzene shows two origin transitions. AM1 calculations (cf. Table II) indicate that the planar-anti conformation 2 is the global minimum and that the planar-syn conformation is significantly destabilized due to steric interactions. From these observations, we conclude that, under the conditions of our supersonic expansion, the molecular conformations detected for ethoxybenzene correspond to 2, i.e., $\tau_1 = \tau(C_{ortho}–C_{ipso}–O–C_\beta) = 0°$ and $\tau_2 = \tau(C_{ipso}–O–C_\beta–C_\gamma) = 180°$. Finally, none of the spectroscopic data obtained in this study suggests the presence of any minor conformational components.

Acknowledgment. We thank Dr. N. Jensen for obtaining the high-resolution mass spectral results.

Registry No. 1, 103-73-1; 4, 29051-95-4; 5, 134334-08-0; 6, 134334-09-1; 7, 134334-10-4; 8a, 99-93-4; 8b, 1676-63-7; 9a, 134334-11-5; 9b, 134334-13-7; 10, 134334-12-6; 11, 621-32-9; 14, 1585-06-4; BrC_2D_5, 3675-63-6; phenol, 108-95-2; o-cresol, 95-48-7.

Supplementary Material Available: Table III (potential contour map of ethoxybenzene), experimental details for the synthesis of 4–7, and the ^{1}H and ^{13}C NMR spectra of these componds (12 pages). Ordering information is given on any current masthead page.