Conformational Analysis through Selective Isotopic Substitution: Supersonic Jet Spectroscopic Determination of the Minimum Energy Conformation of *o*-Xylene

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Supersonic jet mass resolved excitation spectroscopy is employed to observe the $S_1 \leftarrow S_0$ electronic transition origin of the individual conformations of [α-$^2H_1$]-, [α,α-$^2H_2$]- and [α,α′-$^2H_2$]-*o*-xylene and to establish the minimum energy conformation of *o*-xylene in its ground (S_0) and first excited (S_1) singlet states. The *anti*, planar, gear clashed conformer **5** [see Tables 1 and 2; *i.e.*, τ(C-2–C-1–C-α–H-α) = τ(C-1–C-2–C-α′–H-α′) = 180°] is found to be the most stable.

Supersonic jet mass resolved excitation spectroscopy (MRES) has been found to be a superb technique for conformational analysis of substituted aromatic compounds.[1] Each stable ground state conformation of a molecule possesses a unique $S_1 \leftarrow S_0$ origin transition which reflects the zero point vibrational motions within the molecule. MRES of asymmetrically substituted aromatics (*e.g.* ethyl-,[1a] propyl-,[1b] methoxy-[1c] and hydroxymethyl-benzenes[1d]) together with 'structural logic' has allowed conformational analysis of these molecules. We report here the results of a novel and important extension of MRES for the determination of chemical structure.

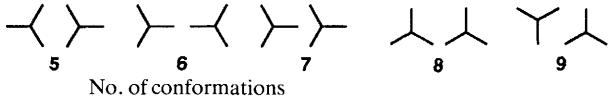
Symmetry inequivalent hydrogens within a molecule each can be expected to possess a unique and distinct potential energy surface.[2] Selective deuteriation within such a set of hydrogens results in a zero point vibrational energy change characteristic of the particular potential energy surfaces (bond) probed by that deuteriation. For example, if a methyl group containing two symmetry inequivalent hydrogen sites is singly deuteriated, and if the distribution of isotopes is statistical within that structure, then a bulk sample of this molecule will contain two species with different zero point energies in a ratio of 2 to 1. In this way, each isotopomer† of a molecule possesses an energetically unique $S_1 \leftarrow S_0$ electronic origin transition. Specifically, MRES can be employed to characterize spectroscopic transitions for the individual isotopomers of *o*-xylene **1**, [α-$^2H_1$]*o*-xylene **2**, [α,α-$^2H_2$]*o*-xylene **3**, and [α,α′-$^2H_2$]*o*-xylene **4**. As is demonstrated below, such a data set can lead to the assignment of a minimum energy structure for *o*-xylene in both its S_0 and S_1 electronic states.

Fig. 1 shows the $S_1 \leftarrow S_0$ origin region of the isotopologues† **1–4**. Only one feature is present for the undeuteriated **1**, Fig. 1(*a*), which indicates that a single conformation obtains for **1**. In addition, the lack of a Franck–Condon progression shows that the S_1 geometry[1e] is essentially unchanged from the S_0 geometry. Recall that the methyl groups are not free to rotate in either S_1 or S_0 in this system: the **1e–1e** transition thus has the same energy as the **1a–1a** 0_0^0 transition.[1] In contrast, the MRES of [α-$^2H_1$]*o*-xylene **2** in Fig. 1(*b*) shows two features separated by 8 cm^{-1}, both blue shifted relative to the origin transition for *o*-xylene itself. Table 1 illustrates a number of possible conformations of *o*-xylene, together with the predicted number and intensity of origin features for isotopologues **2–4**. *Ab initio* calculations[3] show conformation **6** to be a maximum on the potential energy surface; thus **6** is excluded from further consideration (Table 2). Of the remaining conformations, only the predicted relative intensities and number of transitions for **5**, having C_{2V} symmetry, match the experimental results.‡ The relative intensity of the two features in Fig. 1(*b*) is approximately 1 : 2, consistent with the fact that **5** has two in-plane and four *gauche* protons. *Gauche* deuteriation shifts the $S_1 \leftarrow S_0$ transition *ca.* 8 cm^{-1} to the blue, relative to the shift obtained from in-plane deuteriation.

The MRES of [α,α-$^2H_2$]*o*-xylene **3** is essentially the mirror image of the MRES found for **2** [compare Figs. 1(*b*) and (*c*)], consistent with the greater blue shift due to a *gauche* deuteriation and the statistical weight of the intensities. Additional substantiation for the assignment of **5** can be found in the MRES of [α,α′-$^2H_2$]*o*-xylene **4** presented in Fig. 1(*d*). Four origin transitions are observed in an intensity ratio of 1 : 4 : 2 : 2 (see Table 1).

Ab initio calculations on the five conformations **5–9** using the STO-3G,[3] 3-21G* and 6-31G** minimal and split-valence basis sets are consistent with the MRES results. The STO-3G optimized geometry for **5–9** is employed as initial input for geometry optimization with the larger basis sets: geometry optimization is performed for all bond distances, angles and torsional angles except for the six torsional angles which define the methyl groups. The results, shown in Table 2, are consistent among the different basis sets, with **5** being the

Table 1 Conformations proposed for *o*-xylene



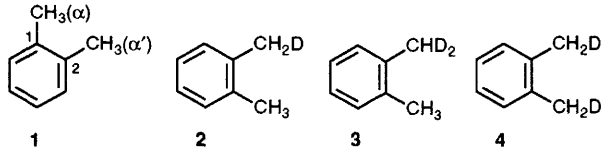
5 **6** **7** **8** **9**

	No. of conformations				
	Predicted				Observed
	5,6	**7**	**8**	**9**	
1	1	1	1	1	1
2	2	4	3	3	2
3	2	4	3	3	2
4	4	4	6	6	4

Table 2 Relative energy in cm^{-1} of specific conformations

	STO-3G	3-21G*	6-31G**	φ[e](°)
5[a]	0[c,d]	0	0	0.404
6[b]	965	1024	1047	3.833
7	407	472	463	1.813
8	528	581	578	2.191
9	416	494	466	1.691

[a] Energy minimum. [b] Energy maximum. [c] Similar results are reported in ref. 3. [d] 1 kcal $mol^{-1} \approx 350$ cm^{-1}. [e] See **10**.



1 **2** **3** **4**

† 'Isotopomers' ('isotopic isomers') are species that are constitutionally and/or stereochemically isomeric because of isotopic substitution. In contrast, 'isotopologues' ('isotopic homologues') are species that differ solely in isotopic content. These distinctions first arose in discussions with J. B. Paine, III.

‡ A detailed microwave study (ref. 4) has previously shown that the minimum energy conformation of *o*-xylene in the ground state is **5**.

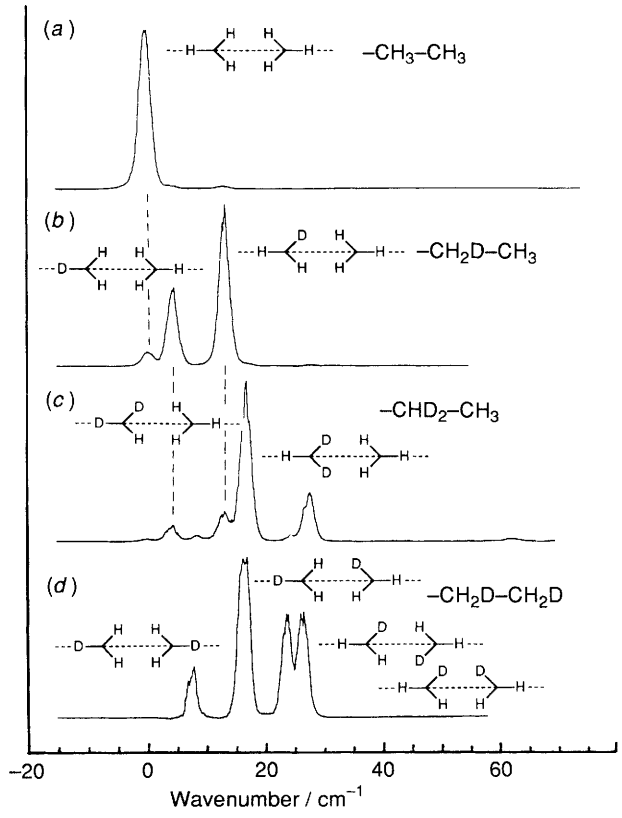
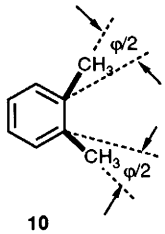


Fig. 1 Mass resolved excitation spectra of *o*-xylene (*a*), [α-$^2H_1$]*o*-xylene (*b*), [α,α-$^2H_2$]*o*-xylene (*c*) and [α,α′-$^2H_2$]*o*-xylene (*d*). The number of features observed for each isotopic species is consistent with structure **5** for *o*-xylene. The features are assigned in the figure to specific isotopomers based on intensity, statistical weights and relative position. Features connected by dashed lines between different spectra are due to detector saturation and ringing from the lower mass to higher mass channels.

ground state energy minimum and **6** being the energy maximum. Also shown in Table 2 is $\phi \equiv 2[\angle(\text{C-2–C-1–C-}\alpha) - 120°]$ the total distortion of the methyl carbons away from



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hexagonal geometry. The minimum value of φ is found for structure **5**, suggesting that the relative stability of **5** is associated with the minimization of short range steric repulsive destabilizing interactions between the two methyl groups.

In summary, these results demonstrate that the minimum energy conformation of *o*-xylene in both the ground and first excited single state is **5**. In addition, MRES is found to be a novel and powerful technique: chemical structure can be directly and straightforwardly identified by examining the spectra of deuteriated species.

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References

1 (*a*) P. J. Breen, E. R. Bernstein and J. I. Seeman, *J. Chem. Phys.*, 1987, **87**, 3269; (*b*) P. J. Breen, J. A. Warren, E. R. Bernstein and J. I. Seeman, *J. Chem. Phys.*, 1987, **87**, 1927; (*c*) P. J. Breen, E. R. Bernstein, J. I. Seeman and H. V. Secor, *J. Am. Chem. Soc.*, 1989, **111**, 1958; (*d*) H.-S. Im, E. R. Bernstein, H. V. Secor and J. I. Seeman, *J. Am. Chem. Soc.*, 1991, **113**, 4422; V. H. Grassian, E. R. Bernstein, H. V. Secor and J. I. Seeman, *J. Phys. Chem.*, 1990, **94**, 6691.

2 J. I. Steinfeld, *Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy*, MIT University Press, Cambridge, MA, 1985; G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrad, Princeton, NJ, 1977; D. G. Lister, J.N. Macdonald and N. L. Owen, *Internal Rotation and Inversion: An Introduction to Large Amplitude Motions in Molecules*, Academic Press, New York, 1978.

3 K. M. Gough, B. R. Henry and T. A. Wildman, *J. Mol. Struct.*, 1985, **124**, 71.

4 H. D. Rudolph, K. Walzer and I. Krutzik, *J. Mol. Spectrosc.*, 1973, **47**, 314.