Observation and Geometry Assignment of Individual Conformations of Aryl Methyl Ethers in the Gas Phase

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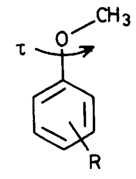
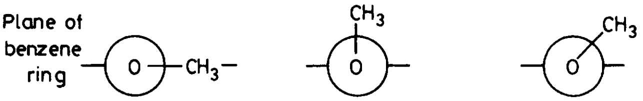
Supersonic molecular jet laser spectroscopy is used to observe the individual conformations of a number of aryl methyl ethers in the gas phase and to establish their planar conformations.

Aromatic methyl ethers continue to play an important role in organic chemistry. This functionality has much synthetic utility and is frequently found in natural products, including many compounds of pharmacological value. The study of the potential energy profiles of this functional group has added significance in terms of regiochemistry; *e.g.*, kinetic electrophilic attack on the aromatic ring system of (**1**) is a function of π-electron density which itself is modified by methoxy conformer distributions.[1] Results from sophisticated experimental and theoretical investigations have been interpreted in terms of planar conformations (*cf.* Scheme 1), though exceptions have been noted and definitive evidence is not available.[2—7]

As part of our studies[8,9] on the conformations and reactivities of aromatic compounds in the gas phase and in clusters, we have examined the supersonic molecular jet laser spectroscopy of anisole and some of its derivatives. The various techniques associated with supersonic molecular jet laser spectroscopy [including one and two colour time of flight mass spectroscopy (TOFMS), fluorescence excitation (FE), and dispersed emission (DE) spectroscopy] employed in these investigations have recently been reported.[9] Consider an aromatic molecule. The energy of the $\pi \rightarrow \pi^*$ electronic transition ($S_1 \leftarrow S_0$) for each stable conformation of the molecule will, in principle, generate its own spectroscopic 0_0^0 transition (origin transition). The converse is also true; *i.e.*,



(1)



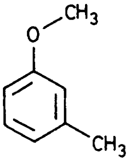
(2) planar

(3) perpendicular

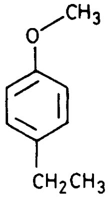
(4) gauche

	No. of conformations			
	Predicted			Observed
Compound	(2)	(3)	(4)	
Anisole (**1**; R = H)	1	1	1	1
3-Methylanisole (**5**)	2	1	2	2
4-Ethylanisole (**6**)	1	2	2	1

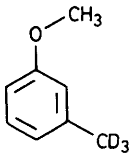
Scheme 1



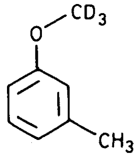
(5)



(6)



(7)



(8)

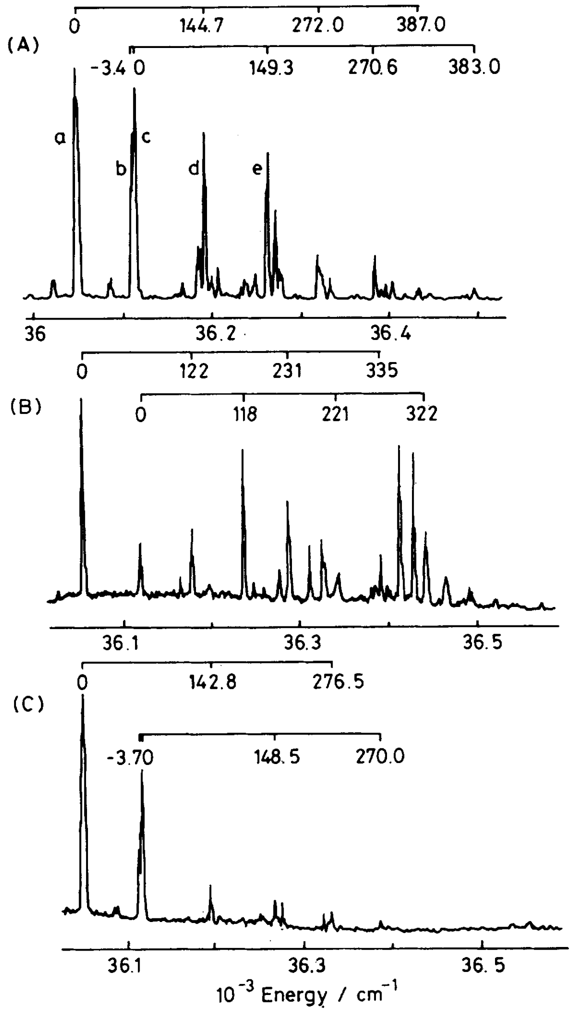


Figure 1. TOFMS of the 0_0^0 region of (A) 3-methylanisole (**5**); (B) 1-methoxy-3-trideuteriomethylbenzene (**7**); and (C) 1-trideuteriomethoxy-3-methylbenzene (**8**). In (A), the features labelled 'a' and 'b' at 36 047.5 and 36 113.8 cm^{-1} are assigned as origins belonging to distinct conformations of the molecule. The ring methyl rotor in S_1 experiences a large barrier to rotation and is responsible for the indicated progressions of peaks on the two origins. In (B), deuteriation of the ring methyl group reduces the spacings between the peaks in the two progressions, proving that these features are indeed due to torsional transitions of the ring methyl group. In (C), deuteriation of the methoxy group has no effect on the spacings of the features relative to those in (A), proving that the transitions between internal rotational states of the methoxy group do not appear in the spectrum.

each origin is associated with a specific stable conformation. Thus, the TOFMS of a jet-cooled compound will contain as many origin transition peaks as there are stable conformations. In this communication, we report the observation of conformational energy minima and geometry assignments for anisole and some simple derivatives.

The TOFMS for jet-cooled anisole (**1**, R = H) using 30 psig of argon as the carrier gas is featureless except for a single origin at 36 381.1 cm^{-1}, thereby providing strong evidence that only one minimum energy conformation exists for an aromatic methyl ether under the expansion conditions. Three different conformations can be proposed: the planar (**2**), perpendicular (**3**), and/or *gauche* (**4**), as shown in Scheme 1. Assignments can be made according to the 'structural logic' contained in Scheme 1, already established by our work on the 1,3- and 1,4-diethylbenzenes.[8,9] By 'structural logic' we imply two distinct lines of reasoning: first, symmetry considerations of the various possible relative orientations of the groups attached to the aromatic ring; and second, potential energy considerations suggesting the energy difference(s) between the various possible structurally nonequivalent conformations.

We have therefore examined the TOFMS of four alkyl substituted anisoles (**5**)—(**8**). The TOFMS of the 0_0^0 region for $S_1 \leftarrow S_0$ of jet-cooled 3-methylanisole (**5**) is presented in Figure 1(A). The most intense and lowest energy feature at 36 047.5 cm^{-1} is readily identifiable as an origin. A series of intense features follows the origin to higher energy. These are most likely due to torsional motion of either the methoxy group or the ring methyl group approaching the harmonic (higher barrier) limit, since the features occur at fairly regular intervals.

Because molecular vibrations and internal rotations have fairly substantial isotope effects,[10] transitions between internal rotational states of the methyl rotor can, in principle, show significant changes in spacings and intensities for the CD_3 analogue. Thus, a comparison of the TOFMS of 3-methylanisole with that of its deuteriated analogues (**7**) and (**8**) allows one to distinguish between $S_1 \leftarrow S_0$ origin transitions for specific ground state energy minima and transitions between internal rotational states of the methyl rotor(s).

Figures 1(B) and 1(C) illustrate the TOFMS of (**7**) and (**8**) respectively. Note that the TOFMS of (**5**), (**7**), and (**8**) all contain a feature *ca.* 64 cm^{-1} to higher energy of the origin. As deuteriation has not caused this feature to shift in energy, the '64 cm^{-1}' feature must be due to a separate origin (conformation). The remaining features do shift in energy on deuteriation, and are thus associated with torsional transitions of the methyl group(s).

As shown in Scheme 1, the observation of two origins for 3-methylanisole excludes the perpendicular conformation (**3**) but does not distinguish between the planar (**2**) and the *gauche* (**4**) conformations. For this differentiation, the TOFMS was determined for 4-ethylanisole (**6**) for which one 0^0_0 (origin) transition is observed.† As shown in Scheme 1, the *gauche* conformation (**4**) is thus eliminated from contention. The data for (**5**)—(**8**) and 1,4-dimethoxybenzene‡ *in toto* are consistent only with the planar conformation (**2**).

One can also obtain potential energy surfaces for the various internal torsional motions that these molecules possess. The observed spectra can be fitted with a one-dimensional rigid rotor model for both methyl and methoxy internal hindered rotor motion. The potential surface shape and parameters will be discussed elsewhere; the theoretical background for such an analysis has recently appeared.[6,7]

These results demonstrate the capability of supersonic molecular jet laser spectroscopy to observe specific molecular conformations which, because they have very low barriers to conformational interconversion, have not previously been observed. Further, based on simple symmetry considerations, the geometry of the minimum energy conformations can be assigned. In the case at hand, individual conformations of aryl methyl ethers have been observed, spectroscopic properties obtained, and their planar geometries established.

We thank R. Ferguson, B. La Roy, and A. C. Lilly for their support and encouragement and J. Campbell for technical assistance.

Received, 17th August 1987; Com. 1212

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† For ethylbenzene, previous studies have demonstrated that $\tau(C_{ortho}-C_{ipso}-C_\alpha-C_\beta)$ = *ca.* 90° where C_α and C_β are the methylene and methyl carbons respectively of the ethyl substituent. For details and leading references, see refs. 8 and 9.

‡ Two rotational isomers of 1,4-dimethoxybenzene (**9**) were observed and assigned by Oikawa *et al.*[6] by molecular jet spectroscopy. Since the syn-planar and syn-perpendicular conformations of (**9**) have identical symmetries (both C_{2v}), the anti-planar and anti-perpendicular conformations of (**9**) have identical symmetries (both C_{2h}), and both planar and perpendicular conformations of (**9**) would yield two and only two origins, conformational assignments based on the report of Oikawa *et al.*[6] would be inclusive.

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