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The rotational spectra, electric dipole moments and molecular structures of anisole and benzaldehyde†

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Received 21st January 2005, Accepted 8th March 2005
First published as an Advance Article on the web 17th March 2005

The rotational spectra of anisole and of benzaldehyde were investigated in supersonic expansion at frequencies up to 41 GHz, and at room temperature in the millimetre-wave region, from 170 to 330 GHz. Accurate spectroscopic constants for the parent isotopomers in the ground vibrational state and for the first excited torsional state were determined for both molecules. The supersonic expansion spectrum allowed measurement, in natural abundance, of all singly substituted ^{13}C isotopomers, as well as of the ^{18}O isotopomer for both anisole and benzaldehyde. The rotational constants were used to determine the r_s and the $r_m^{(1)}$ gas-phase geometries, which are found to be consistent with prediction of bond length alternation in the phenyl ring induced by the asymmetric substituent. Stark measurements were made on the supersonic expansion spectrum resulting in electric dipole moment determination, $|\mu_a| = 2.9061(22)$ D, $|\mu_b| = 1.1883(10)$ D, $\mu_{\rm tot} = 3.1397(24)$ D for benzaldehyde and $|\mu_a| = 0.6937(12)$ D, $|\mu_b| = 1.0547(8)$ D, $\mu_{\rm tot} = 1.2623(14)$ D for anisole. During the investigation it was found that use of a carrier gas mixture consisting of 30% Ar in He carries significant advantages for studies of weak lines, and pertinent experimental details are reported.

1. Introduction

Anisole (methoxybenzene) and benzaldehyde, Fig. 1, are two well known monosubstituted benzene derivatives, which are similar in that both have an asymmetric substituent attached to the phenyl ring. These molecules are of considerable interest from the viewpoint of understanding fundamental molecular properties, benchmarking *ab initio* calculations, and possible environmental monitoring. It suffices to say that in the case of benzaldehyde there is still an apparent factor of 2 discrepancy between theory and experimental deductions concerning the height of the barrier to internal rotation.[1]

Another point of interest is alternation of C–C bond lengths in the phenyl ring introduced by substituents which are asymmetric with respect to the substitution axis. The substituent may cause an imbalance between the two principal canonical structures of the molecule leading to alternation which, in the most favourable cases, reaches the 0.01 Å level. It is not surprising that while this effect is well substantiated by *ab initio* calculations it is rather elusive experimentally. The term Angular-Group Induced Bond Alternation or the AGIBA effect[2,3] has been proposed to describe and to rationalise this behaviour, and its further experimental manifestations are still being sought. The sensitivity of contemporary rotational spectroscopy allows such issues to be addressed with some efficiency. This is due to the fact that supersonic expansion techniques allow rotational spectra of rare isotopomers arising from single substitution of most of the chemically important elements to be observed in natural abundance. The experimental results can contemporarily be augmented by general and efficient least-squares fitting codes of molecular geometry and the success of such techniques has been demonstrated, for example, in the determination of the geometry of camphor.[4] From a survey of the calculated magnitudes of the AGIBA effect in singly substituted phenyl derivatives[2] it transpires that anisole and benzaldehyde would be useful candidates for studying the effect. The effect would be maximised in anisole, while it would be appreciably smaller, but of opposed phase in benzaldehyde. Both molecules should be amenable to determination of the heavy atom geometry by rotational spectroscopy of the natural abundance samples, since the abundances of the atoms involved, ^{13}C (1.1%) and ^{18}O (0.2%), are within the sensitivity of the technique.[4]

Finally, even though larger ring molecules are conspicuously absent in lists of interstellar molecules detected by radioastronomy,[5,6] there has been considerable interest in small aromatic molecules arising from postulated appreciable abundance of polyaromatic hydrocarbon (PAH) molecules in space.[7,8] Such molecules have also featured in discussions of the longest-standing astrophysical spectroscopic mystery of the Diffuse Interstellar Bands.[9] Previous studies of the rotational spectrum of anisole[10] and of benzaldehyde[11] do not provide sufficient information for possible radioastronomical searches. The reported results have been limited to sub-40 GHz measurements on room-temperature samples. Only the parent isotopomer was measured and the determined spectroscopic constants do not depart much from rigid rotor analysis. In this work we report the results of comprehensive investigation of the rotational spectra of the two title molecules, from the centimetre-wave region to the submillimetre-wave region.

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† Electronic supplementary information (ESI) available: Measured and fitted field-free transition frequencies, frequencies of Stark components, and substitution Cartesian coordinates. See http://www.rsc.org/suppdata/cp/b5/b501041a/

DOI: 10.1039/b501041a

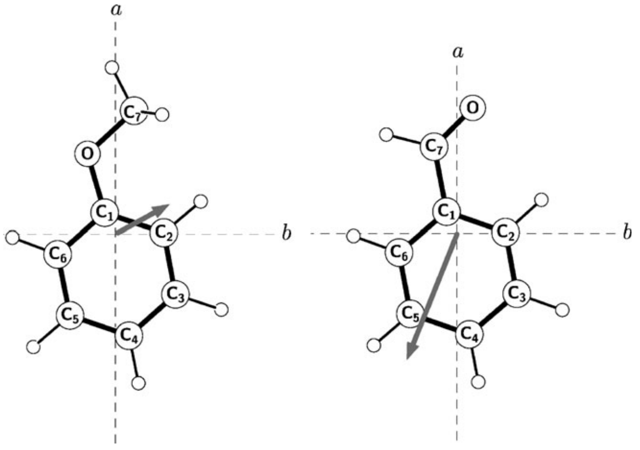

Fig. 1 The molecular geometry of anisole and of benzaldehyde, orientation of the principal axes, dipole moment vectors and atom labelling.

2. Experimental

Rotational spectra were recorded using commercial samples, and three different spectrometers. Most of the low frequency rotational spectra, including those of the rare isotopomers were measured in supersonic expansion using the Flygare-type, cavity, Fourier-transform microwave (FTMW) spectrometer in Warsaw.[12] The sample was held in a small stainless-steel test tube placed close to the pulsed expansion nozzle, and in the path of Ar carrier gas injected at a backing pressure of *ca.* 1.2 atm. The sample was pulsed at a rate of 3 Hz in a direction perpendicular to the axis of the Fabry-Perot cavity. This configuration corresponds to that of the original Balle-Flygare spectrometer,[14] and it is more convenient for Stark measurements. Frequency coverage of this spectrometer is 2–18.5 GHz. Additional supersonic-expansion FTMW measurements on benzaldehyde, were made using the spectrometer at Harvard,[13] and extended up to 41 GHz. In this case, a mixture of benzaldehyde in Ne as buffer gas was used. The backing pressure was 3.5 atm and the repetition rate of the nozzle was 6 Hz. The orientation of the molecular beam was parallel to the axis of the Fabry-Perot cavity of the spectrometer, which is a configuration that ensures maximum sensitivity. In both spectrometers sample dilution in carrier gas was 1% or less.

Millimetre-wave (MMW) spectra were measured at room-temperature and at a sample pressure of 20–30 mTorr with the broadband, BWO-based, source-modulation spectrometer in Warsaw described in refs. 15 and 16, and in references cited therein.

The Warsaw FTMW spectrometer was also used to make Stark measurements by employing a custom arrangement of modified parallel plate electrodes.[17,18] The electrodes were designed using numerical electric field calculations to produce uniform electric field at the large electrode separation required to not perturb the microwave modes in the Fabry-Perot resonator.[17] Electric field calibrations were made on the basis of the $J = 1 \leftarrow 0$ transitions of CH_3CN, $\mu = 3.921\,97(13)$ D,[19] and of CH_3I, $\mu = 1.6406(4)$ D.[20] Stark measurements were fitted with program QSTARK, which has been described in ref. 17 and is available from the PROSPE database.[21]

In optimising the performance of the Warsaw spectrometer for measuring weak lines of the rare isotopomers we have found a new set of useful experimental conditions. The importance of the choice of carrier gas on the strength and lineshape of the supersonic expansion FTMW signal is well known and has been addressed on several occasions.[22–24] One aims for a compromise between signal strength, the magnitude of the Doppler splitting and, for spectra of molecules, mitigation of signal loss arising from formation of too many intermolecular complexes. The best choice seems to be the use of Ne carrier gas.[22] The only disadvantage is cost, and for this reason the use of "first run" Ne (*i.e.* 70% Ne : 30% He) has been a popular alternative.[23] It appears that an even more affordable mixture is possible, requiring the use of only the two cheapest noble gases. This is documented in Fig. 2, which displays both the original interferograms and their Fourier transforms as a function of expansion mixture composition. Considerable care has been taken in keeping the conditions constant, including the timings involved in preparing each mixture. The signal of the parent isotopomer line in Fig. 2 is near the spectrometer saturation level so that intensity changes are not reliable, but this line serves to illustrate the nature of the recorded interferogram. The Doppler doubling has the effect of splitting the interferogram into wavepackets of sharply decreasing intensity—two of which are visible in this case. For weak signals the second wavepacket becomes lost in noise, while the length of the first wavepacket decreases rapidly with increasing Doppler doubling. If only this wavepacket can reasonably be used in the FFT then the consequences are a much broader line and decreased frequency measurement accuracy. Thus even though in our experimental configuration the use of pure He leads to superior signals than with pure Ar this is actually associated with a loss in performance. This is evidenced, for example, by the apparent frequency shift in the He only spectra for the two

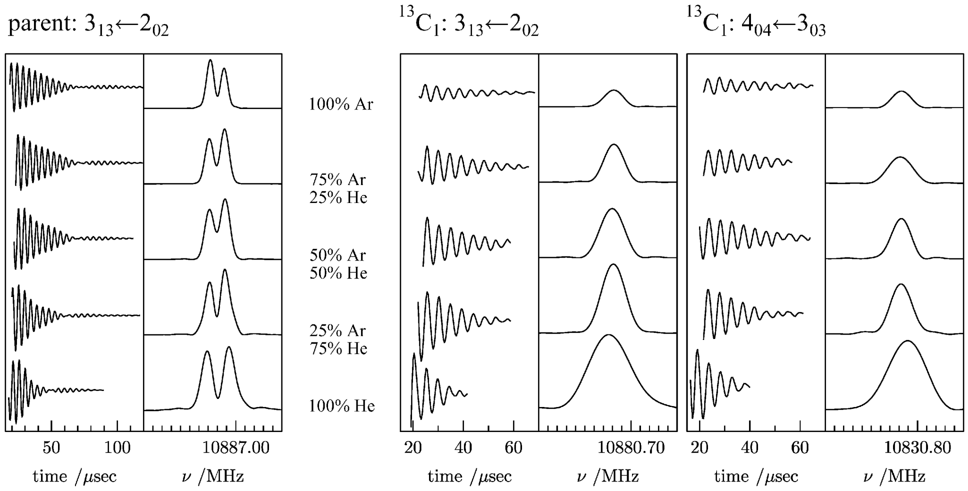

Fig. 2 The influence of the composition of the buffer gas on intensity and lineshapes of anisole transitions observed with the cavity, supersonic-expansion FTMW spectrometer in Warsaw. Note the several-fold increase in the intensity of the signal for both *a*-type, and *b*-type transitions of the ^{13}C isotopomer on changing from pure Ar to pure He carrier gas. The observation of only a moderate increase in linewidth for compositions containing as little as 25% of Ar recommends the use of such mixtures in practical applications.

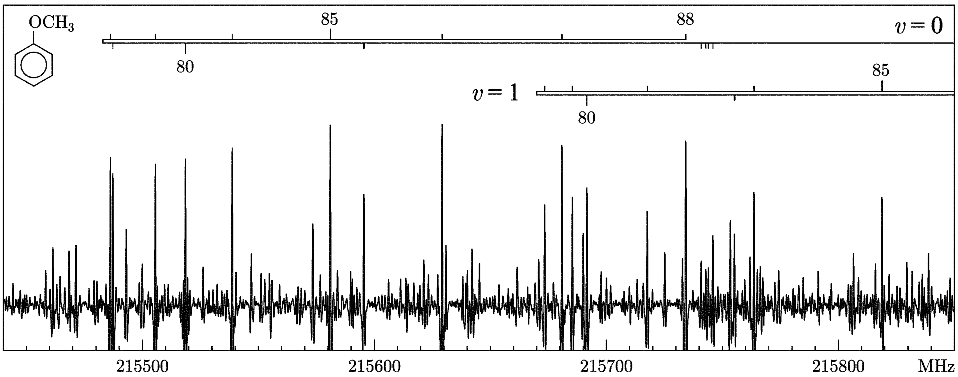

Fig. 3 The room-temperature millimetre wave spectrum of benzaldehyde. Each line in the two visible bands results from an overlap of a pair of strong ^aR-type, and a pair of much weaker ^bR-type transitions with a common value of J'', marked on the diagram.

^{13}C isotopomers in Fig. 2. Fortunately if a He/Ar mixture is employed, there appears to be a useful compromise at about 3 : 1 He : Ar composition for which there is a considerable gain in signal, at a cost of only of a minimal increase in the Doppler doubling. This suggests that the kinematics of the molecular expansion, as evident from the magnitude of the Doppler doubling (or the linewidth), is still dominated by the heavier carrier gas component. On the other hand the thermodynamics of the cooling appears to be proportional to the average carrier gas composition. With this mixture intensity gain by a factor of 3 to 5 has been observed for weak rotational transitions in both anisole and benzaldehyde, as well as for several other molecules. There were, however, some molecules for which this effect was not significant, and studies correlating signal gain with features of intramolecular dynamics are still in progress. The transferability of this technique between experimental configurations is also not clear but it does, nevertheless, appear to be a promising experimental tool.

3. Rotational spectrum

The millimetre wave rotational spectra were studied first, by using predictions made on the basis of published centimetre-wave data.[10,11] For both molecules the ground state spectrum was expected to be accompanied by that in a low lying first excited state of the torsional vibration, which is only about 100 cm^{-1} above the ground state. Benzaldehyde is planar, and anisole is near-planar, in that only two hydrogen atoms lie out of the ring plane. For this reason high-J rotational spectra of the two molecules were expected to be characterised by type-II$^+$ bands, which arise from specific overlaps of ^aR- and ^bR-type transitions.[25,26] The overlaps are such that consecutive lines away from the band-head are characterised by values of J decreasing by 1 and values of K_{-1} increasing by 2. The properties of such bands have been studied in detail,[25–27] are well understood, and are of considerable help in assigning the millimetre wave spectrum.[28] Representative bands of this type are shown in Fig. 3 for benzaldehyde, and in Fig. 4 for anisole. Bands for the ground state and for the torsional state are clearly visible. The folding back of such bands occurs for negative values of the inertial defect, Δ_i, and is proportional to its magnitude. Thus the ground state band for benzaldehyde, $\Delta_i = -0.113$ u Å^2 shows just the onset of this effect, the torsional excited state of benzaldehyde, $\Delta_i = -1.001$ u Å^2 shows marked folding, while even the ground state band for anisole, $\Delta_i = -3.409$ u Å^2 is subject to considerable folding. Measurements of band lines allowed location of ^bQ-type transitions for both molecules, and were finally augmented by low-J measurements made at the sub-Doppler conditions of supersonic expansion. The datasets were combined with previous measurements, where available, and are reported in Tables S1 and S2 (see ESI†) for ground and first excited torsional states of benzaldehyde, respectively, and in Tables S3 and S4 (see ESI†) for the corresponding states in anisole. The measurements were fitted with Watson's A-reduced Hamiltonian in representation I^{r}[29] and the resulting constants are reported in Table 1. For both molecules there is a similar negative change in the inertial defect between the ground and the excited torsional state. The magnitude of the quartic defect for anisole and benzaldehyde is comparable with 0.003 81(9) MHz^2 for fluorobenzene.[31] Benzaldehyde is planar and anisole non-planar and this is reflected in the value of the inertial defect, but not so in the quartic defect. The vibrational change in the quartic defect is also different for the two molecules.

Determination of accurate constants for the parent isotopomers of benzaldehyde and of anisole facilitated searches for

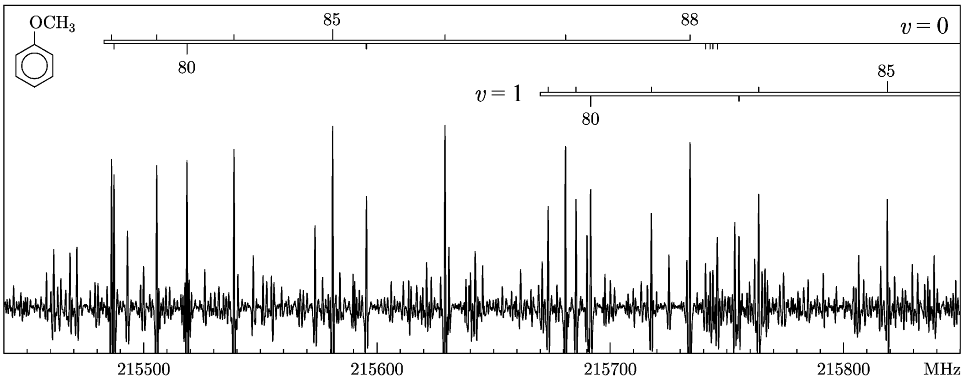

Fig. 4 The room-temperature millimetre wave spectrum of anisole. The observed bands are for the same values of the quantum number J''as in Fig. 3, although in this case each line results from an overlap of a pair of strong ^bR-type transitions, and a somewhat weaker pair of ^aR-type transitions. The differences between line distribution in bands of anisole and benzaldehyde arise from the difference in the inertial defect between the two molecules.

Table 1 Spectroscopic constants for the ground and for the excited torsional state of benzaldehyde and of anisole

	Benzaldehyde		Anisole	
	Ground state	$v = 1$	Ground state	$v = 1$
A/MHz	5234.364 365(54)[a]	5213.169 69(58)	5028.844 14(19)	5015.724 83(22)
B/MHz	1564.274 377(22)	1564.930 28(17)	1569.364 308(68)	1569.376 40(14)
C/MHz	1204.681 915(16)	1206.494 318(87)	1205.825 614(41)	1207.419 747(66)
Δ_J/kHz	0.068 564 9(35)	0.069 871(12)	0.060 3743(39)	0.061 4774(83)
Δ_{JK}/kHz	0.162 745(28)	0.159 46(11)	0.041 045(33)	0.041 014(54)
Δ_K/kHz	0.739 45(16)	0.648 98(52)	0.783 354(67)	0.776 97(17)
δ_J/kHz	0.017 959 1(14)	0.018 1813(61)	0.015 9437(18)	0.016 0516(45)
δ_K/kHz	0.289 28(11)	0.275 72(21)	0.179 228(90)	0.175 74(12)
Δ_i[b] (u Å^2)	−0.113 490(7)	−1.000 81(5)	−3.409 40(2)	−4.223 13(4)
Δ_q[c]/MHz^2	0.004 45(8)	−0.002 20(17)	−0.002 61(7)	−0.001 89(10)
N_{lines}	387	211	154	135
σ_{fit}/kHz	68.3	98.1	39.7	38.8
σ_w[d]	0.755	0.892	0.799	0.775

[a] The quantities in parentheses are standard errors in units of the least significant digit of the value of the constant. [b] Inertial defect, $\Delta_i = I_c - I_a - I_b$. [c] Quartic defect, $\Delta_q = 4C\Delta_J - (B - C)\Delta_{JK} - 2(2A + B + C)\delta_J + 2(B - C)\delta_K$, ref. 30. [d] Root mean square deviation of a weighted fit assuming 2 kHz frequency accuracy for FTMW, 50 kHz for MMW measurements. In addition, lines from ref. 11 for benzaldehyde were weighted with 100 kHz for the Wyoming spectrometer, and with 200 kHz for the Oklahoma spectrometer.

Table 2 Rotational constants for the ground states of the seven singly substituted ^{13}C isotopomers and for the ^{18}O isotopomer of benzaldehyde

	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$
A/MHz	5231.8257(11)	5170.794(17)	5140.865(10)	5230.851(16)
B/MHz	1563.207 463(11)	1564.315 15(18)	1555.486 60(14)	1540.231 25(15)
C/MHz	1203.917 994(10)	1201.304 92(17)	1194.481 68(13)	1190.193 17(14)
N_{lines}	6	6	7	6
σ_{fit}/kHz	0.08	1.4	1.2	1.1

	$^{13}C_5$	$^{13}C_6$	$^{13}C_7$	^{18}O
A/MHz	5176.494(11)	5145.957(14)	5221.040(12)	5222.119(19)
B/MHz	1549.046 64(17)	1563.497 55(15)	1546.321 14(15)	1492.774 49(27)
C/MHz	1192.583 20(14)	1199.476 36(14)	1193.315 13(15)	1161.221 45(22)
N_{lines}	6	6	7	7
σ_{fit}/kHz	1.2	1.1	1.3	1.7

rotational spectra of rare isotopomers by using the same natural abundance samples. As in the camphor study[4] the isotopomers were searched for in order of increasing distance of the substituted atom from the centre of mass. Spectral predictions were made on the basis of MP2/6-31G(d,p) *ab initio* geometries calculated with the PC-GAMESS version[32] of the GAMESS package.[33] In order to improve prediction accuracy the calculated geometries were scaled with a single scaling factor chosen to reproduce the rotational constants for the parent isotopomers. Furthermore, the search for the ^{18}O isotopomers, which are more than 5 times weaker than the ^{13}C isotopomers, was only attempted once a preliminary experimental geometry was determined. The number and the types of rotational transitions required for reliable determination of all three rotational constants was also carefully optimised. For each isotopomer 6 to 7 rotational transitions were measured such that they comprise a mixture of *a*-type and *b*-type transitions. The data files are collected in Table S5 (see ESI†) for the measured rare isotopomers of benzaldehyde, and in Table S6 (see ESI†) for anisole. The fitted rotational constants are reported in Tables 2 and 3. In all cases the values of the centrifugal distortion constants determined for the pertinent parent isotopomer were assumed. The deviations of the fit are all within the nominal 2 kHz frequency accuracy of the spectrometer. The anomalously low uncertainties in rotational constants for the $^{13}C_1$ isotopomer of benzaldehyde are a consequence of the number of transitions in the dataset being too small for reliable operation of statistics. It is more likely that the actual uncertainties in constants for this isotopomer are an order of magnitude greater and closer to the level evident for the other isotopomers in Table 2.

4. Molecular structure

The rotational constants determined above can be used, in the first instance, to determine the substitution, r_s, geometry of the heavy atom backbone of both molecules. In the case of benzaldehyde rotational constants for deuterium substitution of the aldehydic proton at C_7 are also available.[11] ‡ The use of Kraitchman equations,[34,35] leads to coordinates reported in Table S9 (see ESI†). The coordinates carry the errors suggested by Costain[36] to provide a realistic account of the uncertainties from vibration–rotation effects. The error on coordinate z is

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‡ For use in this work the original measurements were refitted by assuming the values of the quartic centrifugal distortion constants from an *ab initio* calculation, resulting in $A = 5105.84(8)$, $B = 1540.6643(17)$, and $C = 1183.8976(15)$ MHz.

Table 3 Rotational constants for the ground states of the seven singly substituted ^{13}C isotopomers and for the ^{18}O isotopomer of anisole

	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$
A/MHz	5026.2317(22)	4971.1629(14)	4941.3969(17)	5024.4815(17)
B/MHz	1568.322 78(45)	1569.397 00(30)	1560.671 71(36)	1544.894 01(33)
C/MHz	1205.062 81(20)	1202.500 59(13)	1195.630 19(16)	1191.082 83(14)
N_{lines}	6	6	6	6
σ_{fit}/kHz	1.3	0.8	1.0	1.1

	$^{13}C_5$	$^{13}C_6$	$^{13}C_7$	^{18}O
A/MHz	4978.7261(27)	4947.3917(27)	5020.6029(27)	4992.9008(27)
B/MHz	1553.661 17(54)	1568.442 49(56)	1533.156 30(53)	1539.147 05(61)
C/MHz	1193.673 65(24)	1200.539 19(25)	1183.879 44(24)	1185.897 83(30)
N_{lines}	6	6	6	6
σ_{fit}/kHz	1.5	1.6	1.6	1.2

thus given by $\delta z = 0.0015/|z|$ Å. The resulting r_s values of various structural parameters are reported in Table 4. Unfortunately, it turns out that the r_s evaluation is subject to several types of pathological behaviour. First of all, atom C_2 in both molecules is sufficiently close to the b axis (see Fig. 1) that its substitution a-coordinate is imaginary and appreciable, at $0.082i$ Å for anisole and $0.092i$ Å for benzaldehyde. For this reason none of the internal coordinates involving this atom can be evaluated. Furthermore, addition of a moderately light, but asymmetric substituent onto the phenyl ring has the effect of introducing a small rotation between the ring and the inertial axes, with the consequence that several other atoms also have small inertial coordinates. The most affected of those atoms are C_1 and C_4, and the associated small coordinates degrade the accuracy of many of the reported r_s parameters.

A global, least-squares fit to all available rotational constants is normally expected to average over such problems. Unfortunately in the present case the pathological behaviour turns out to be sufficiently severe that even a meaningful ground state, r_0, geometry cannot be determined. Additional hindrance is introduced by the presence of the vibrational inertial defect which, though small, cannot be accounted for by this method. The solution is to evaluate the r_z,[35] and even better the recent version of the r_m geometry.[38] The latter has been shown to deliver equilibrium-quality geometries for many small molecules[38] and intermolecular complexes,[39] and has also been found to be successful in the case of the much larger camphor molecule.[4] This is the type of geometry that is most directly comparable with results of *ab initio* calculations, which are evaluated at equilibrium. A general computer program, STRFIT, implementing this method is also available.[39,21] The results of fitting the $r_m^{(1)}$ geometry are summarised in Table 4, in which they are compared with the electron diffraction geometry available for benzaldehyde,[37] and with results of

Table 4 Comparison of experimental and calculated geometrical parameters (Å and °) for anisole and benzaldehyde

	Anisole			Benzaldehyde			
	r_s	$r_m^{(1)}$	*Ab initio*[a]	r_g[b]	r_s	$r_m^{(1)}$	*Ab initio*[a]
$r(C_1C_2)$	—	1.387(4)	1.399	1.398(5)	—	1.391(4)	1.401
$r(C_1C_6)$	1.391(6)	1.396(4)	1.401	1.398	1.384(6)	1.390(5)	1.399
$r(C_2C_3)$	—	1.407(4)	1.399	1.390(8)	—	1.399(5)	1.392
$r(C_5C_6)$	1.398(4)	1.392(3)	1.390	1.390	1.404(4)	1.399(4)	1.395
$r(C_3C_4)$	1.396(4)	1.391(3)	1.392	1.397(12)	1.404(5)	1.398(3)	1.400
$r(C_4C_5)$	1.394(5)	1.398(3)	1.399	1.397	1.389(6)	1.395(4)	1.396
$r(C_1O)$	1.381(4)	1.372(3)	1.372				
$r(C_7O)$	1.418(3)	1.417(2)	1.422	1.212(3)	1.212(4)	1.213(3)	1.227
$r(C_1C_7)$				1.479(4)	1.498(4)	1.492(3)	1.480
$r(C_7H)$				1.109(19)	1.111(3)	1.102(3)	1.106
$\angle(C_6C_1C_2)$	—	121.1(3)	120.1	119.9(7)	—	121.4(3)	120.3
$\angle(C_1C_2C_3)$	—	118.7(3)	119.2	120.2(10)	—	119.0(4)	119.6
$\angle(C_1C_6C_5)$	118.9(6)	119.5(2)	120.0	120.2	119.1(6)	119.6(2)	119.9
$\angle(C_2C_3C_4)$	—	121.0(1)	121.0	119.5(6)	—	120.1(2)	120.1
$\angle(C_4C_5C_6)$	120.6(6)	120.5(1)	120.4	119.5	119.7(6)	119.6(1)	119.8
$\angle(C_3C_4C_5)$	119.1(5)	119.2(1)	119.3	120.7(5)	120.3(5)	120.3(1)	120.2
$\angle(C_6C_1O)$	114.0(5)	114.8(3)	115.1				
$\angle(C_1OC_7)$	117.2(4)	117.5(3)	116.6				
$\angle(C_6C_1C_7)$					118.1(6)	118.7(4)	119.7
$\angle(C_1C_7O)$				123.6(4)	124.4(5)	124.3(3)	124.3
$\angle(C_1C_7H)$					115.3(5)	115.2(3)	115.0
c_α[c]/(u$^{1/2}$ Å)		0.0219(3)				0.0157(3)	
σ_{fit}[d]/(u Å^2)		0.0036				0.0040	

[a] Evaluated at the MP2/6-31G(d,p) level. [b] Geometry from electron diffraction ref. 37. Symmetry of the phenyl ring about the C_1C_4 axis was assumed. [c] Fitted using the assumption $c_a = c_b = c_c$. [d] Standard deviation of fit to 27 moments of inertia for anisole and 30 moments of inertia for benzaldehyde.

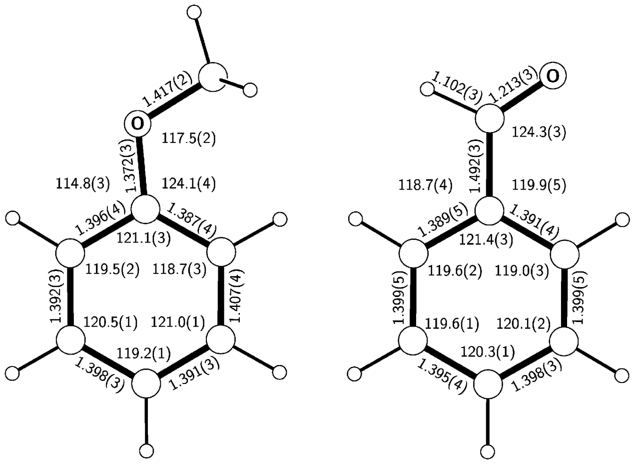

Fig. 5 Summary of the $r_m^{(1)}$ molecular geometry determined for anisole (left) and for benzaldehyde (right).

ab initio calculations. With the exception of the aldehydic proton in benzaldehyde only heavy atom substitution was investigated, so that several subsidiary assumptions concerning the geometry of the CH bonds have been required. All $\angle$(HCC) were taken from the MP2/6-31G(d,p) calculation. The values of r(CH) were estimated by using the approximate scaling $r(\mathrm{MP2}) + [r(\mathrm{MP2}) - r(\mathrm{HF})]/4$ of MP2 and Hartree–Fock results for the 6-31G(d,p) basis set, suggested by the systematic comparison between experimental and *ab initio* results.[40] Finally, in order to use such bond lengths within the $r_m^{(1)}$ model, the δ_H parameter for all r(CH) was fixed at the mean value of 0.01 Å determined from results for diatomic molecules.[38] For a complete heavy atom skeleton a total of 13 independent parameters need to be determined for each molecule, with an additional 2 parameters required for location of the aldehydic proton in benzaldehyde. There are a total of 27 moments of inertia for anisole and 30 for benzaldehyde available for this purpose. It turns out, however, that the number of available degrees of freedom is still insufficient for a numerically stable fit with the use of all three different c_α constants of the $r_m^{(1)}$ model. Since these results showed that the values of all three of these constants are rather similar, the assumption $c_a = c_b = c_c$ was employed.

The quality of the $r_m^{(1)}$ fit obtained for both molecules is excellent and corresponds to sub-0.1 MHz reproduction of the experimental rotational constants. The determined $r_m^{(1)}$ structural parameters, and in particular the angles, represent a significant improvement in precision over the corresponding r_s values, as well as over the electron diffraction result for benzaldehyde. The comparison with *ab initio* values is on the whole satisfactory, and some appreciable differences are also understood. For example the experimental r_g, r_s, and $r_m^{(1)}$ values for $r(\mathrm{C{=}O})$ in benzaldehyde are in good agreement with each other, but appreciably shorter than the calculation, as is generally observed.[40] The longer experimental $r(\mathrm{C_1C_7})$ in benzaldehyde than from calculation is probably another manifestation of the same effect, namely of the deficiency in the calculated electron density distribution at C_7. The issue of bond length alternation turns out to be not easily resolvable since magnitudes of the experimental errors are about half the maximum calculated bond length difference for adjacent bonds. It is probably easier to discern a pattern in the measured values rather than to compare tabulated numbers, and for this reason Fig. 5 has been drawn as an aid to reading Table 4. A clear bond alternation is visible for anisole, in that $r(\mathrm{C_1C_6}) > r(\mathrm{C_1C_2})$, $r(\mathrm{C_2C_3}) > r(\mathrm{C_5C_6})$, and $r(\mathrm{C_4C_5}) > r(\mathrm{C_3C_4})$. These relationships are also all consistent with the trends in relative values predicted by the *ab initio* calculation. In contrast, the experimental results for benzaldehyde do not exhibit any appreciable bond length alternation, and bond lengths in pairs discussed above are practically the same. We note, however, that the *ab initio* geometry for benzaldehyde also exhibits much smaller differences between lengths of adjacent CC bonds in the phenyl ring than in anisole. Thus the much more uniform experimental benzaldehyde geometry might also be considered to be supportive of the argument that the aldehyde group induces a much smaller AGIBA effect than the methoxy group. It should be noted that, irrespective of the finer features in the distortions in the phenyl ring on substitution, the major effect is an appreciable increase in the value of $\angle \mathrm{C_2C_1C_6}$ from 120° in both molecules. This is accompanied by different behaviour on the opposed side of the ring. For anisole $\angle \mathrm{C_4C_5C_6}$ decreases relative to 120°, while an increase in this angle is apparent for benzaldehyde. Also if we compare the deviations from 120° of the ring angles at C_1, C_2, C_3, and C_4, we presently obtain for anisole 1.1, −1.3, 1.0, and −0.8°, respectively. These values are in fair agreement with angular substitution changes induced by the methoxy group of 0.2, −0.6, 1.1, and −1.1°, respectively, derived from a least squares fit to results from X-ray crystallography obtained for many aromatic molecules.[41]

5. Electric dipole moment

Precise determinations of the electric dipole moment of benzaldehyde and of anisole were carried out by means of the Stark effect measured at conditions of supersonic expansion. In the case of anisole the positions of a total of four Stark lobes were measured in two different rotational transitions, the b-type $3_{13} \leftarrow 2_{02}$ transition and the a-type $4_{04} \leftarrow 3_{03}$ transition. For benzaldehyde a total of six different Stark lobes in three rotational transitions, $4_{14} \leftarrow 3_{13}$, $4_{04} \leftarrow 3_{03}$, and $4_{14} \leftarrow 3_{03}$ were measured. The measurements were fitted by using the program QSTARK from the PROSPE website,[21] and the results are summarised in Table 5. Standard deviations of the fits are comparable to the nominal 2 kHz accuracy of the FTMW spectrometer. The quality of the fits can also be inspected graphically in the plots in Fig. 6, and the measured Stark lobes are seen to exhibit almost pure second order behaviour. This is relatively rare at the conditions of high-resolution Stark measurements possible with the Warsaw

Table 5 Comparison of the measured and calculated values for the electric dipole moment of benzaldehyde and anisole

	Benzaldehyde				Anisole			
	Measured	HF[a]	MP2[a]	B3LYP[a]	Measured	HF	MP2	B3LYP
$\lvert\mu_a\rvert$ (D)	2.9061(22)[b]	3.15	2.81	3.09	0.6937(12)	0.60	0.65	0.76
$\lvert\mu_b\rvert$ (D)	1.1883(10)	1.45	1.14	1.11	1.0547(8)	1.51	1.15	1.08
$\lvert\mu_c\rvert$ (D)	3.1397(24)	3.47	3.03	3.28	1.2623(14)	1.63	1.32	1.32
N_t, N_s[c]	3,36				2,28			
σ_{fit}/kHz	1.96				0.93			

[a] Using the 6-31G(d,p) basis set. [b] The cited error accounts for both the standard deviation from the fit, and a conservative estimate of the error in electric field calibration. [c] N_t is the number of different rotational transitions investigated, and N_s is the total number of fitted Stark measurements, respectively.

Table 6 Comparison of the measured values of spectroscopic observables for anisole and benzaldehyde with values calculated from the *ab initio* harmonic force field

	Benzaldehyde			Anisole		
	Exp.	MP2[a]	DFT[b]	Exp.	MP2[a]	DFT[b]
Δ_J/kHz	0.068 5649(35)	0.0681	0.0681	0.060 3743(39)	0.0650	0.0615
Δ_{JK}/kHz	0.162 745(28)	0.160	0.169	0.041 045(33)	0.0374	0.0357
Δ_K/kHz	0.739 45(16)	0.733	0.728	0.783 354(67)	0.821	0.795
δ_J/kHz	0.017 9591(14)	0.0180	0.0179	0.015 9437(18)	0.0174	0.0164
δ_K/kHz	0.289 28(11)	0.285	0.289	0.179 228(90)	0.190	0.184
$\Delta_i(v = 0)$/u Å^2	−0.113 490(7)	−0.127	−0.063	−3.409 40(2)	−3.464	−3.417
$\Delta_i(v = 1)$/u Å^2	−1.000 81(5)	−1.020	−0.959	−4.223 13(4)	−4.374	−4.254
$E(v = 1)$/cm^{-1}	113.8(50)[c]	110.0	122.0	83.0(37)[d]	81.0	92.0

[a] MP2/6-31G(d,p) force field, scaled by 0.9 (0.95 in frequency). [b] B3LYP/6-31G(d,p) force field, scaled by 0.96 (0.98 in frequency). [c] Ref. 11. [d] Ref. 10.

spectrometer,[17] when even a small amount of mixed order behaviour is visible. In the present case only the $3_{13} \leftarrow 2_{02}$, $M = 2$ component of anisole shows minimal curvature. The actual experimental data are listed in Tables S7 and S8 (see ESI†). The dipole moments of both molecules have been measured at the 0.1% level, and most of the reported uncertainty arises from a conservative estimate of the electric field calibration. It has been the practice in this laboratory to increase this several-fold relative to its least squares estimate, in order to account for several factors outside direct experimental control that might have a bearing on Stark measurements.[18]

The orientations and the relative magnitudes of the experimental dipole moments of anisole and benzaldehyde are plotted in Fig. 1, where dipole moment directions (from negative to positive) have been assumed on the basis of *ab initio* calculations. It is directly apparent that the dipole moment of each molecule is strongly correlated with the direction and the expected polarisation of the C–O bond in that molecule. Table 5 also presents a comparison of measured values with the results of *ab initio* calculations carried out with the popular 6-31G(d,p) basis set. While MP2 and the B3LYP levels of calculation are both superior to the simple HF calculation, the patterns of deviations for both molecules are different and do not allow a straightforward rationalisation. The present results allow the reliability of some previous dipole moment values for the two molecules to be assessed. For benzaldehyde the previously reported gas-phase total dipole moment of 3.21(4) D[42] is in agreement with the present value of 3.140(2) D at the 2σ level. Liquid phase dipole determinations for benzaldehyde, at 2.73–2.99 D,[43] are systematically lower than the value for the isolated molecule. For anisole the reported gas-phase value of 1.38(7) D,[44] is again in agreement with the present value of 1.2623(14) within its 2σ bounds, which are admittedly rather generous.

6. Discussion

The results of the present investigation allow accurate predictions of the rotational spectra of the two title molecules well into the sub-millimetre region. Spectroscopic constants are augmented by accurate values of dipole moments, thus creating a sound basis for possible teledetection applications. Observation of rare isotopomers allowed determination of hitherto most precise molecular geometries for the two molecules. The achieved level of accuracy is still lower than would be desirable for a confident discussion of bond alternation in the phenyl ring. Nevertheless, the present results are generally supportive of the presence of an appreciable AGIBA effect in anisole, and of a much smaller magnitude of such behaviour in benzaldehyde. One may attempt to reduce the effect of experimental

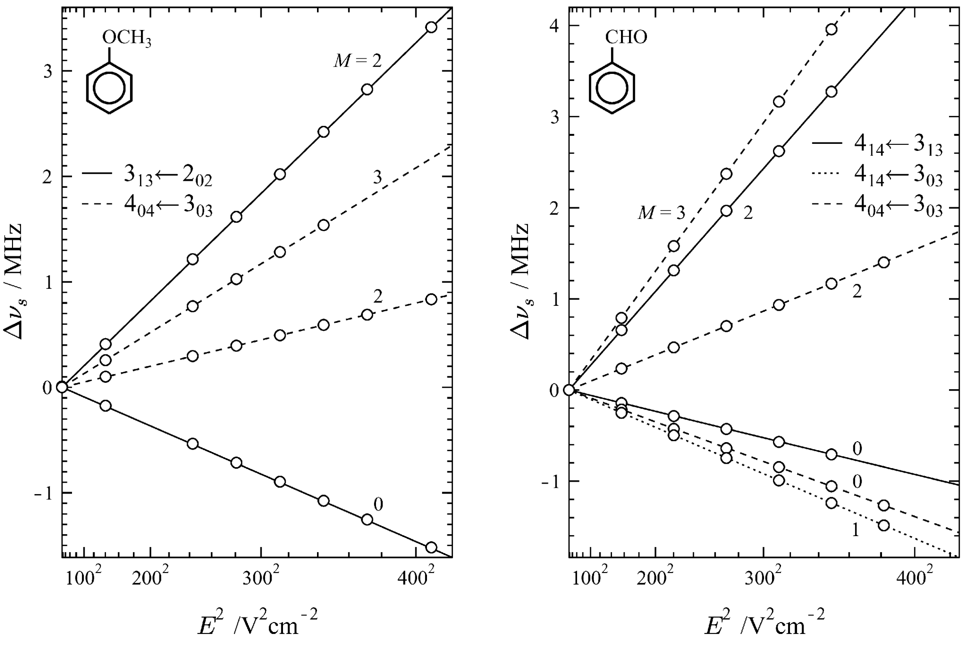

Fig. 6 Summary of Stark effect measurements for selected *a*-type and *b*-type rotational transitions of anisole (left) and benzaldehyde (right).

errors, by considering the average bond distance b_1 for the C_1–C_2, C_3–C_4, C_5–C_6 bonds, and b_2 for the C_2–C_3, C_4–C_5, C_1–C_6 bonds. For anisole $b_1 = 1.390$ Å, $b_2 = 1.400$ Å, while for benzaldehyde $b_1 = 1.396$ Å, $b_2 = 1.395$ Å. These values are consistent with present and previous[2,3] *ab initio* predictions of both the relative magnitude and the phase of the AGIBA effect in the two molecules. The only previous experimental study of this effect in singly substituted benzene derivatives has been made on the basis of crystal diffraction data available for 21 diazo-derivatives of benzene.[45]

Finally, precise determination of the several spectroscopic observables dependent on the harmonic force field enables a test of the computational methods used by spectroscopists to predict/rationalise such results. Table 6 presents a suitable comparison concerning quartic centrifugal distortion constants, inertial defects and the vibrational frequency of the torsional mode. Two of the most popular levels of computation for this size of problem are tested, at customarily employed force field scaling. The required calculations were performed with program VIBCA.[21] The comparison with experiment is excellent, but it does not appear to favour any particular method, even though on the basis of empirical knowledge the DFT results would be expected to be superior for dealing with observables involving low frequency vibrations. The MP2 results are somewhat better for benzaldehyde, while DFT fares better for anisole. It is useful to note that the inertial defects for the ground and the torsional excited state are equally well predicted for both planar benzaldehyde and for the non-planar anisole, since this quantity is one of the most useful tools in assigning excited vibrational states in the rotational spectrum.[31]

Acknowledgements

Financial support from the Institute of Physics and from the State Committee for Scientific Research, grant KBN-1-PO3B-055-26 is gratefully acknowledged. One of the authors (ST) is indebted to the Alexander von Humboldt-Foundation for a Feodor Lynen research fellowship.

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