Characterization of Rotameric Mixtures in *o*- and *m*-Substituted Benzaldehydes by Matrix Isolation IR Spectroscopy

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The cis and trans conformers of benzaldehydes substituted in the *o*- or *m*-positions by Cl or CN can be differentiated by IR spectroscopy in Argon matrices. Partial photochemical rotamerization allows assignment of the IR bands and establishment of their relative intensities in pairs of rotamers, which permits, in turn, quantitation of equilibrium compositions prior to photolysis. The observed spectra and equilibrium compositions are in very good agreement with the predictions of vibrational spectra and free energy differences from B3LYP/6-31G* calculations. The present work represents the first attempt to quantitate the small contributions that the cis rotamers make to the room-temperature equilibrium compositions of the two *o*-substituted benzaldehydes. The results for the *m*-substituted derivatives are compared to earlier estimates based on other methods.

Introduction

Rotational isomerism in *o*- and *m*-substituted benzaldehydes has attracted a great deal of attention, and many experimental techniques have been applied to gain insight into this question. In particular, measurements of electric dipole moments[1−4] and polarizabilites,[2] NMR,[5−11] IR,[12−15] and emission spectra,[16,17] as well as gas-phase electron diffraction patterns[18] have been used to assess the equilibrium composition of the two rotamers. However, agreement between the different estimates of conformational abundance obtained from various methods leaves much to be desired. On the other hand, computational studies on the title question published so far are limited to early semiempirical[19,20] or ab initio

calculations at the SCF level,[9,10,18,20] the latter often with minimal basis sets. We therefore decided to re-address this question with new experimental and theoretical methodology. As substrates we chose *o*- and *m*-chloro benzaldehyde, about which quite a bit of information is already available from earlier studies,[2,3,8,12−14,16,18] and the corresponding cyano derivatives, whose rotameric behavior has been much less investigated.[3,10]

o-cis   *o*-trans   *m*-cis   *m*-trans

X=Cl, CN
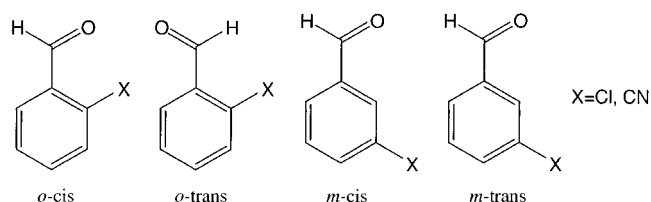
Experimental and Theoretical Methods

Samples of the four compounds (from Aldrich, used without further purification) were placed in a U-tube attached to the inlet system of a closed-cycle cryostat where they were swept along by a stream of high-purity Argon passing over them and trapped on a CsI window held at ca. 19 K during the matrix deposition. It has been demonstrated that by this technique the conformational mixture that prevails in the gas phase is quenched in the matrix.[21,22] The U-tube was immersed into a bath whose temperature was adjusted in a series of trial experiments such that an appropriate amount of the substrate was contained in a matrix obtained by condensing about 80 Torr of Ar from a 2.2 L flask over a period of 2 h. After deposition, the sample was cooled to the lowest temperature attainable with the cryostat, ca. 12 K. To obtain IR spectra, 256 scans were accumulated at 1 cm^{-1} resolution on a Bomem DA3 interferometer equipped with an MCT detector and a KBr beam splitter. After this, the rotameric equilibrium was shifted by irradiation of the samples for 150 min with an Ar plasma lamp through a 295 nm cutoff filter.

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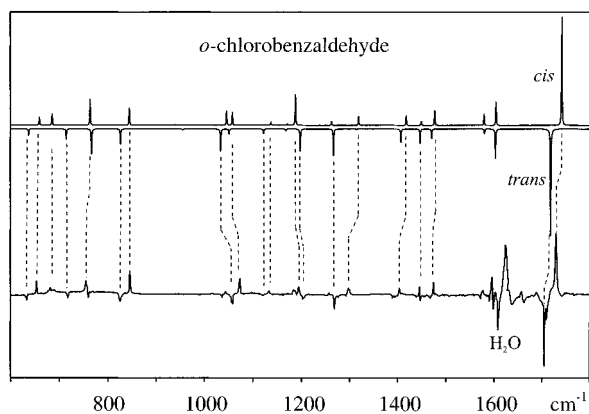
Figure 1. Bottom: Difference spectrum for >295 nm irradiation of *o*-chlorobenzaldehyde in an Ar matrix. Top: Spectra of the cis and trans rotamers of *o*-chlorobenzaldehyde calculated by B3LYP/6-31G* (all frequencies scaled by 0.96).

Geometries of the cis and trans rotamers (carbonyl group relative to the substituent) of the four compounds were optimized with the B3LYP/6-31G* method,[23,24] which was also used subsequently to compute second derivatives from which vibrational frequencies and IR intensities were obtained. The structures and vibrational frequencies were also used to calculate thermal corrections and entropies, so the computed energy differences could be converted into ΔG^ϑ(298 K). All calculations were effected with the Gaussian program package.[25]

Results and Discussion

Due to differences in the absorptivities of cis and trans rotamers, their ratio in the matrix (which is assumed to be that which prevails in the gas-phase just prior to trapping on the cold window of the cryostat) cannot be obtained from the absolute spectra. However, the changes in the concentrations of the two rotamers that can be induced by UV irradiation of the samples, in conjunction with the accompanying quantum chemical model calculations, permit an assignment of bands and an assessment of their relative intensities in pairs of rotamers. This allows, in turn, calculation of the equilibrium composition from the absolute spectra measured prior to photolysis.

The spectra shown at the bottom of Figures 1−4 represent the difference after and before irradiation of the samples at >295 nm until a photostationary equilibrium was reached. In all cases except in *m*-chlorobenzaldehyde where the changes were found to be very small, these difference spectra reveal clear changes in the composition of the samples. At the top of each Figure, the spectra calculated for the cis and trans rotamers of the different compounds are shown. For better comparison, these spectra are presented in such a way that the
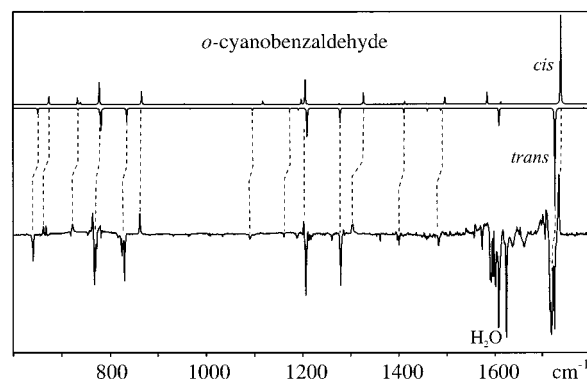
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Figure 2. Bottom: Difference spectrum for >295 nm irradiation of *o*-cyanobenzaldehyde in an Ar matrix. Top: Spectra of the cis and trans rotamers of *o*-cyanobenzaldehyde calculated by B3LYP/6-31G* (all frequencies scaled by 0.96).
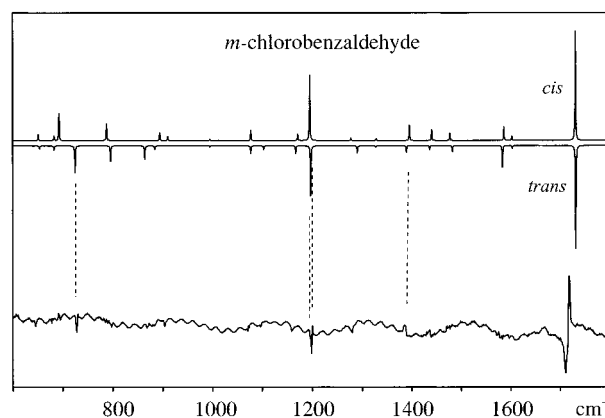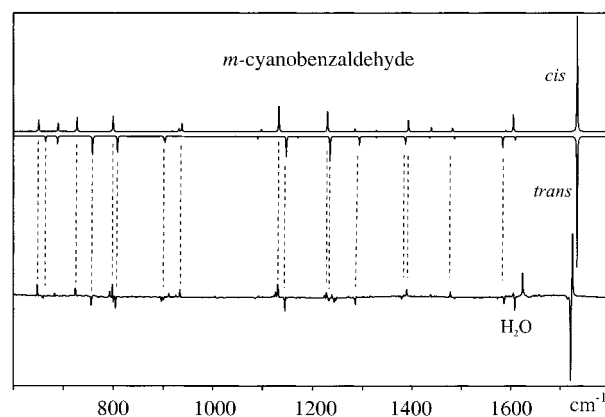

Figure 3. Bottom: Difference spectrum for >295 nm irradiation of *m*-chlorobenzaldehyde in an Ar matrix. Top: Spectra of the cis and trans rotamers of *m*-chlorobenzaldehyde calculated by B3LYP/6-31G* (all frequencies scaled by 0.96).

Figure 4. Bottom: Difference spectrum for >295 nm irradiation of *m*-cyanobenzaldehyde in an Ar matrix. Top: Spectra of the cis and trans rotamers of *m*-cyanobenzaldehyde calculated by B3LYP/6-31G* (all frequencies scaled by 0.96).

peaks pointing down are those of the trans rotmer (which is depleted in the course of the photolyses), whereas those of the cis rotamers point upward.

Not unexpectedly, the differences in the spectra for the two rotamers are more pronounced in the *o*-isomers than the *m*-isomers. In particular, the C=O stretching vibrations around 1720 cm^{-1} are shifted by 15−25 cm^{-1} in the *o*-isomers, whereas these shifts are only 3−6 cm^{-1} in the

Table 1. Experimental and Calculated Frequencies of C=O Stretching Vibrations (cm⁻¹)

	experimental		calculated[a]	
benzaldehyde	cis	trans	cis	trans
o-cyano	1734	1719	1739	1727
m-cyano	1725	1721	1736	1735
o-chloro	1730	1705	1741	1718
m-chloro	1718	1712	1732	1733

[a] After scaling the B3LYP/6-31G* frequencies by 0.96.

Table 2. Relative B3LYP/6-31G* Energies (kcal/mol) of the Cis and Trans Rotamers of Cyano- and Chlorobenzaldehydes

benzaldehyde	E(trans)	E(cis)	ΔG(298 K)	trans/cis
o-cyano	0[a]	2.16	2.04	97/3
m-cyano	0[b]	0.24	0.23	60/40
o-chloro	0[c]	2.73	2.59	99/1
m-chloro	0[d]	0.04	0.03	51/49

[a] Total energy = −437.812268 h. [b] Total energy = −437.814068 h. [c] Total energy = −805.165205 h. [d] Total energy = −805.168041 h.
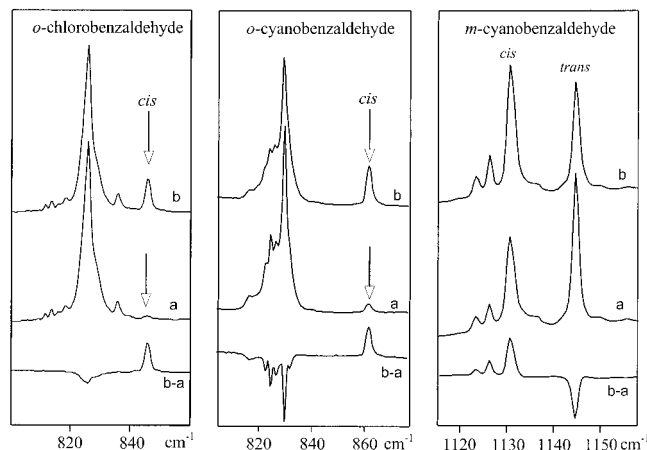

Figure 5. Sections of the spectra of the three compounds indicated at the top that were used in the assessment of the amount of cis rotamer present after deposition of the matrix (spectra a). The decrease in trans rotamer upon >295 nm photolysis was set equal to the increase in cis rotamer (spectra b). The relative integrated peak intensities were obtained from the difference spectra (b − a), which allowed the amount of cis rotamer prior to photolysis to be calculated.

m-substituted benzaldehydes (see Table 1). Nevertheless, due to the general sharpness of the IR peaks in Ar matrices, the shifts are large enough to resolve the two peaks even in the case of the *m*-isomers. Note that the shifts in the C=O stretching vibrations are predicted quite accurately by B3LYP for the *o*-derivatives, whereas they are underestimated for the *m*-derivatives.

In the *m*-substituted benzaldehydes the spectra obtained after trapping the room-temperature rotamer mixture in the matrix indicate that both conformers are clearly present. Although the C=O stretching peaks overlap partially, there are other bands in the spectra that allow quantification of the equilibrium position, at least for the cyano derivative where good difference spectra were obtained. In this compound, a band at 1131 cm⁻¹ that is assigned to the cis rotamer (together with a group of peaks at the low-energy side that are probably due to molecules in different matrix sites) and a peak at 1144 cm⁻¹ of the trans rotamer are sufficiently well separated to allow a quantitative analysis (cf. Figure 5).

Assuming that no side reactions take place upon UV irradiation, peak integration in the difference spectrum shows that the 1123−1133 cm⁻¹ group of peaks of the cis rotamer are 1.5 times more intense than the 1141 cm⁻¹ peak of the trans rotamer (B3LYP predicts a ratio of 1.2 for the corresponding transition moments). Applying this factor to the spectrum measured after deposition of the matrix yields an estimate of 57% trans and 43% cis conformer in *m*-cyanobenzaldehyde. This value is in excellent agreement with the prediction based on the calculated ΔG(298 K) of 0.23 kcal/mol (Table 2) from

which a 60:40 ratio of the two rotamers can be deduced. For the *m*-chloro derivative, only the strong, overlapping C=O stretching vibrations could be assigned unambiguously. The corresponding peaks indicate, however, that the equilibrium constant must be close to unity in this case, again in agreement with the very small calculated value of ΔG(298 K) = 30 cal/mol for this compound.

We can compare our present findings to those from earlier studies. For *m*-chlorobenzaldehyde, percentages of the cis rotamer ranging from 22[14] to 65%[8] had been deduced from measurements of dipole moments,[2,3] molecular Kerr constants,[2] ¹H[5] and ¹³C NMR spectra[8] as well as IR spectra,[14] and gas-phase electron diffraction experiments.[18] Unfortunately, our experiments do not allow placement of precise limits on this number, but the B3LYP calculations indicate that it should not deviate much from 50%.

In the case of the *m*-cyano compound the situation is better in that only two other, less divergent estimates of the equilibrium composition are available. In 1976, Bruce et al. concluded from dipole moment measurements that $35 \pm 2\%$ should be present in the form of the cis rotamer,[3] whereas the more recent study of Schaefer et al., who measured NMR spectra in different solvents, predicted by extrapolation to $\epsilon = 1$ that the proportion of the cis rotamer should be close to 50% in the gas phase. Our experiments and calculations agree in saying that this proportion should lie roughly between these two earlier experimental estimates.

In contrast to the *m*-derivatives, the IR peaks of the cis rotamers that rise on photolysis were found to have only very small intensities in the starting spectra of the *o*-derivatives. Applying the same procedure as described above for the *m*-derivatives to pairs of bands around 840 cm⁻¹ (cf. Figure 5) allowed us to determine that only $1 \pm 0.2\%$ of the *o*-chloro- and $4 \pm 1\%$ of the *o*-cyanobenzaldehyde are initially present in the form of the cis rotamers. This finding is again in very good accord with the results of the B3LYP calculations of the free energy differences (Table 2) from which it can be deduced that 98.8% of the *o*-chloro and 97.5% of the *o*-cyanobenzaldehyde, respectively, should be present in the more stable trans conformation at room temperature. The shifts of the major IR bands on going from trans to cis rotamers are also predicted quite accurately by B3LYP (cf. Table 1).

The above results are again in agreement with earlier findings based on other methods that indicated that the trans rotamers predominate strongly in the room-temperature equilibria of *o*-chloro-[2,7,8,16] and *o*-cyanobenzaldehyde,[3,10] although the present experiments and calculations provide the first quantitative estimates of equilibrium constants. It is interesting to recall that the more polar cis rotamer of the *o*-cyano compound gains in importance on going from the gas phase to solvents with

increasing dielectric constants to attain nearly 50% in acetone.[10] On the theoretical side we note that semi-empirical and minimal basis set ab initio SCF calculations strongly underestimate the energy difference between the two rotamers, whereas calculations with the 6-31G basis set appear to slightly overestimate this difference at the SCF level.[10]

Conclusions

We have been able to assess the ratio of cis to trans rotamers in *o*- and *m*-chloro- and cyanobenzaldehydes, respectively, by measuring their IR spectra, in particular the changes induced by UV irradiation, in Ar matrices at 12 K. Thereby we found for the first time that about 1% of the *o*-chloro and about 4% of the *o*-cyano derivative, respectively, are present in the form of the cis rotamer at room temperature (under the usual assumption that the room-temperature equilibrium is trapped unchanged upon low-temperature matrix isolation). In the *m*-sub-stituted compounds these proportions are much higher (43% in the cyano derivative and about 50% in the chloro derivative). The observed spectra of both rotamers, in particular the shifts between similar bands, are in very good agreement with those calculated at the B3LYP/6-31G* level. This is also true for the cis/trans ratios, which are in excellent accord with those predicted from free energy differences calculated with the same method.

Supporting Information Available: Total energies, Cartesian coordinates, and harmonic vibrational frequencies and intensities as well as thermal corrections for both rotamers of the four compounds studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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