Barrier to Rotation about the Phenyl−Carbonyl Carbon Bond of Methyl Benzoate by Dynamic NMR Spectroscopy and ab Initio Molecular Orbital Calculations

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Received July 20, 1999

Introduction and Background

Rotation about the bond between a benzene ring and a carbonyl group has been studied by dynamic NMR spectroscopy for a number of compounds, including benzaldehydes,[1−3] benzoyl halides,[4] benzoyl cyanide,[4] and acetophenones.[3,5] However the barrier to rotation in methyl benzoate (**1**) does not appear to have been reported. Anet and Ghiaci[4] reported that no dynamic NMR effect was observed at 50.32 MHz in the ^{13}C NMR spectra of **1** at temperatures to −175 °C and noted that failure to observe hindered rotation could be due to either a low barrier to rotation or to a small chemical shift difference between ortho carbons. An attempt by other workers[6] to determine the rotational barrier in ethyl *p*-methoxybenzoate (**2**) by dynamic NMR spectroscopy was described[4] as unsuccessful, but these workers[6] list a free-energy barrier of 4.6 kcal/mol for this compound in a paper published a year later.[3]

Katritzky[7,8] has observed that the barriers to rotation (E) in systems of this type are related to resonance energies and strain energies by eq 1

$$E = R - R_{\mathrm{tw}} - S \qquad (1)$$

in which R and R_{tw} are the resonance energies of the ground state and transition state, respectively, and S is the strain energy of the ground state less that of the transition state (including rehybridization). The resonance interactions in monosubstituted benzenes are proportional to the absolute values of the σ^0_{R} constants, and a proportionality constant of 33 was derived[7] from the free-energy barrier of 7.9 kcal/mol for benzaldehyde[1] and the σ^0_{R} constant of 0.24 for the formyl group, with the assumption that R_{tw} and S are negligible for this compound. A barrier of 5.3 kcal/mol was predicted[8] for methyl benzoate from the σ^0_{R} constant of 0.16 for the carbomethoxy group, again with the assumptions that the resonance interaction between the group and the benzene ring can be neglected in the transition state for rotation and that the ground state is nearly strain free. A free-energy barrier near 5.3 kcal/mol for **1** should be accessible by dynamic NMR spectroscopy provided the chemical shift difference for the ortho carbons is sufficiently large. A low-temperature ^{13}C NMR study at 75.57 MHz was conducted in order to see if this barrier was indeed accessible.

Experimental Section

Methyl benzoate (99%) was purchased from Aldrich Chemical Co. and used as received. A satisfactory level of purity was established by the room-temperature ^{13}C NMR spectrum. A 1% solution of **1** in 3:1:1 $CHClF_2/CHCl_2F/CHF_3$ was prepared in a 5 mm thin-walled NMR tube, which was kept below 0 °C most of the time. *Caution*: high pressure. A small amount of TMS was added for an internal reference. The low-temperature ^{13}C NMR spectra were recorded on a General-Electric Model GN-300 widebore NMR spectrometer, operating at a frequency of 75.57 MHz. Spectra were taken with a 5 mm dual probe, and spinning was discontinued below −120 °C. The sweep width, pulse width, tip angle, delay time, block size, line broadening, and number of acquisitions were ±10 500 Hz, 6 μs, 60°, 1 s, 64 K, 3 Hz, and 600, respectively, except at −182.2 °C, where 324 scans were recorded.

Because of the difficulty in ejecting the sample at the lower temperatures, the temperature calibration was performed separately using a copper−constantan thermocouple immersed in the same solvent mixture contained in a nonspinning dummy sample tube and under conditions as nearly identical as possible. The emf's were measured using a Leeds-Northrup Model 8690-2 millivolt potentiometer, with the decoupler turned off. The uncertainty in the temperatures was estimated to be ±2 °C.

The low-frequency peak for the ortho carbons of **1** was obscured by other signals in the spectrum, and the chemical shift difference for the ortho carbons at −182.2 °C (36.4 Hz) was estimated by extrapolating the averaged shift of these carbons to this temperature and multiplying the separation of this average value and the high-frequency peak by 2. The rate constant for **1** at the coalescence temperature (−170.6 °C) was obtained by line shape matching with an Apple computer and a two-site program written by Newmark.[9] The relaxation time, T_2, for the calculations was obtained from the line width for the para carbon at this temperature.

The initial structure of the *Z* conformation of methyl benzoate was generated and minimized with a default (Sybyl) force field built into a graphical interfacing program, Spartan 3.0, and installed on a Silicon Graphics Iris workstation. The Cartesian coordinates obtained were used to prepare input for the ab initio calculations. Full geometry optimizations, followed by the calculation of harmonic frequencies for the global minimum-energy structures were repeated until the HF/6-311G* and MP2/6-31G* levels were reached. The transition-state structure was obtained by changing the carbon (ortho)−carbon (ipso)−carbon (carbonyl)−oxygen (carbonyl) dihedral angle and applying the QST2 method. The validity of the transition-state structure was tested by the presence of one imaginary frequency at each level. All ab initio calculations were performed on a CRAY C-90 supercomputer using the Gaussian 94 series of programs[10] at the Mississippi Center for Supercomputing Research.

Results and Discussion

The ^{13}C spectrum of **1** at − 80.3 °C shows the expected four peaks for the carbons of the aromatic ring at δ 134.56

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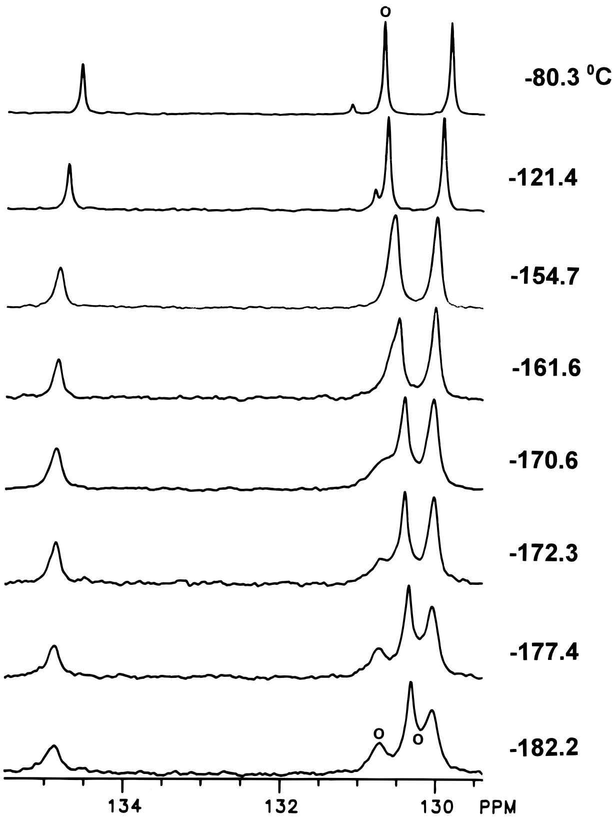

Figure 1. Low-temperature ^{13}C NMR spectra of methyl benzoate in 3:1:1 $CHClF_2/CHCl_2F/CHF_3$.

(para), 131.10 (C_1), 130.68 (ortho), and 129.81 (meta) (Figure 1). The C_2-C_6 chemical shift differences are larger in benzaldehydes[2] and acetophenones[5] than the corresponding C_3-C_5 shift differences, and assignment of the peak at δ 130.68 for **1** to the ortho carbon is based on the observation of decoalescence for this peak at low temperatures, but not for the peak at δ 129.81, assigned to the meta carbons. As the temperature is lowered from −80 °C, the ortho and ipso carbon peaks move to lower frequency, and the peak for the meta carbons moves in the opposite direction. Coalescence of the ortho carbon signal occurs at −170.6 °C, and by −182.2 °C, slow exchange was reached. The low-frequency ortho carbon signal overlaps peaks from the ipso and meta carbons, and its chemical shift was estimated as described in the Experimental Section. The rate constant of 67.0 s^{-1} at −170.6 °C corresponds to a free-energy barrier of 4.92 ± 0.2 kcal/mol at this temperature. This barrier is lower than for related compounds (Table 1) and reflects the importance of cross conjugation of the carbonyl carbon in **1** with the methoxy oxygen. The report[3] of a lower barrier for ethyl *p*-methoxybenzoate (**2**) (4.62 kcal/mol) than for methyl benzoate (4.92 kcal/mol) is surprising, as *p*-methoxy substitution increases the free-energy rotational barriers of benzaldehyde and acetophenone by 1.4 and 1.3 kcal/mol, respectively (Table 1). A spectrometer frequency corresponding to 25.1 MHz for ^{13}C and a solvent mixture of $CHClF_2$ and $CHCl_2F$ were specified[3] for the low-temperature NMR study of **2**, but other details of the study were not given (chemical shift difference; coalescence and slow exchange temperatures). The barrier predicted for **1** by Katritzky's equation (5.3 kcal/mol) is in good agreement with the experimental value. This barrier is based on a constant (33) that related the free-energy barrier[1] of 7.9 kcal/mol for benzaldehyde and the σ^0_R constant of 0.24 for the formyl group; however, the barrier for benzaldehyde was based on a rate constant obtained in an early study[1] from the ^1H NMR spectrum by an approximate method and with vinyl chloride as solvent. A free-energy barrier of 7.58 kcal/mol later obtained[3] from line shape matching of the ^{13}C spectra and with a solvent mixture ($CHClF_2/CF_2Cl_2$) more similar to the one used in the study of **1** might provide a proportionality constant more suitable for estimation of the barrier for methyl benzoate. A constant of 31.6 is obtained from this smaller barrier for benzaldehyde, and with the σ^0_R value for the carbomethoxy group (0.16), a free-energy barrier of 5.06 kcal/mol is predicted for **1**, in excellent agreement with the experiment. Ab initio calculations (Table 2) at the levels used overestimate the rotational barrier. A free-energy barrier of 6.28 kcal/mol was calculated for −182.2 °C at the MP2/6-31G* level.

Table 1. Free-Energy Barriers to Rotation for Some Aromatic Carbonyl Compounds

compound	free-energy barrier (kcal/mol)	solvent	ref
benzaldehyde	7.9	*a*	1
	7.58	*b*	3
	7.65−7.76	*c*	11
p-methoxybenzaldehyde	9.02	*b*	3
acetophenone	5.4	*d*	5
p-methoxyacetophenone	6.7	*d*	5
benzoyl fluoride	7.0	*e*	4
benzoyl cyanide	8.4	*e*	4
methyl benzoate	4.92	*f*	this work
ethyl *p*-methoxybenzoate	4.62	*g*	3

[a] Vinyl chloride. [b] Mixture of $CHCl_2F$ and CF_2Cl_2. [c] Dimethyl ether. [d] 1:1 $CHClF_2/CHCl_2F$. [e] 3:1 $CHClF_2/CHCl_2F$. [f] 3:1:1 $CHClF_2/CHCl_2F/CHF_3$. [g] $CHClF_2/CHCl_2F$.

Table 2. Relative Free Energies[a] and Lowest Frequencies of Methyl Benzoate, at Various Temperatures from Ab Initio Calculations

	HF/6-311G*			MP2/6-31G*		
conformer	25 °C	−182.2 °C	low frequency (cm^{-1})	25 °C	−182.2 °C	low frequency (cm^{-1})
global minimum	0.00	0.00	64.161	0.00	0.00	44.592
transition state	8.24	7.75	83.648 i	6.94	6.28	80.817 i

[a] In kcal/mol.

Acknowledgment. We thank the National Science Foundation (RIMI Grant No. HRD-9450455) and the National Institutes of Health (MBRS Grant No. SO6-GM08047) for support of this work and the Mississippi Center for Supercomputing Research for a generous amount of time on the CRAY C-90 supercomputer. Some calculations were done using the molecular modeling laboratory at Jackson State University, supported by the Army High Performance Computing Research Center.

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