Molecular structure of 1,3-dimethoxybenzene as studied by gas-phase electron diffraction and quantum chemical calculations

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ABSTRACT

The molecular structure and conformational properties of 1,3-dimethoxybenzene (1,3-DMB) have been studied by gas-phase electron diffraction (GED) and quantum chemical calculations (B3LYP and MP2 methods with 6-31G(d,p) and cc-pVTZ basis sets). The differences between geometrical parameters were constrained at values calculated at B3LYP/cc-pVTZ and MP2/cc-pVTZ levels. Quantum chemical calculations predict three stable planar conformers for 1,3-DMB: *syn–anti* (C_s symmetry), *anti–anti* (C_{2v} symmetry), and *syn–syn* (C_{2v} symmetry) with abundances of about 65%, 20%, and 15%, respectively (*syn* and *anti* describe the orientation of the O–CH$_3$ bonds relative to the C1–C2 and C2–C3 bonds, respectively). The GED analysis results in a mixture of 46(19)% *syn–anti*, 31(15)% *anti–anti*, and 23% *syn–syn* conformers, close to the contributions predicted by theoretical calculations. The experimental structural parameters agree well with results of B3LYP/cc-pVTZ and MP2/cc-pVTZ calculations.

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1. Introduction

The conformational preference of the methoxy group in anisole, $C_6H_5OCH_3$, has been studied thoroughly over the years. Both, experimental and recent computational methods [1–5], resulted in a planar conformation. 1,2-Dimethoxybenzene (1,2-DMB) has two methoxy groups in adjacent positions and steric hindrance lead to stabilization of nonplanar conformers. The conformational properties of 1,2-DMB were studied by gas-phase electron diffraction (GED) and quantum chemical calculations in our recent work [6], as well as in some earlier works (see references in [6]). As a part of our studies of the conformational properties of anisole derivatives we present here a GED analysis of 1,3-dimethoxybenzene (1,3-DMB).

The conformation of 1,3-DMB is characterized by the two torsional angles around the C(sp^2)–O bonds, φ_1(C2–C1–O7–C9) and φ_2(C2–C3–O8–C10). For atom numbering see Fig. 1. The three possible planar conformations of 1,3-DMB, *syn–anti* (C_s symmetry), *anti–anti* (C_{2v} symmetry), and *syn–syn* (C_{2v} symmetry) are shown in Fig. 2. *Syn* and *anti* describe the orientation of the O–CH$_3$ bonds relative to the C1–C2 and C2–C3 bonds, respectively.

The available experimental and theoretical data on conformational composition of 1,3-DMB are ambiguous. The photoelectron spectrum of 1,3-DMB was interpreted in terms of a planar *anti–anti*

structure based on results of HF/STO-3G calculations [7]. On the other hand, optical spectroscopic data were associated with three planar structures of 1,3-DMB, without giving any relative contributions [8]. The conformational equilibrium in 1,3-DMB was also studied using the non-linear dielectric effect method [9]. The results were interpreted in terms of a conformational equilibrium of *syn–anti* ($\sim$85%) and *syn–syn* ($\sim$15%) conformers.

The geometry for the *syn–anti* conformer of 1,3-DMB was fully optimized and the dipole moment was calculated at the HF/STO-3G level of theory [10]. From the difference between calculated and experimental dipole moments it was suggested that all planar conformers may contribute to the measured dipole moment, according to their respective equilibrium statistical weights. Very recently the B3LYP/6-311++G(d,p) calculations have been reported which result in three stable planar conformers with the *syn–anti* structure to be lowest in energy and the *anti–anti* and *syn–syn* forms higher by 0.5 and 0.7 kcal/mol, respectively [5].

In the present study, the gas-phase structure and conformational composition of 1,3-DMB have been investigated by means of GED and quantum chemical calculations.

2. Quantum chemical calculations

In the first step the two-dimensional energy surface as a function of the two torsional angles φ_1 and φ_2 in steps of 30° was calculated by the MP2/6-31G(d) method (Fig. 3). Three minima with $\varphi_1/\varphi_2 = 0°/180°$, 180°/180°, and 0°/0° on the potential energy surface correspond to the planar *syn–anti*, *anti–anti*, and *syn–syn* conformers,
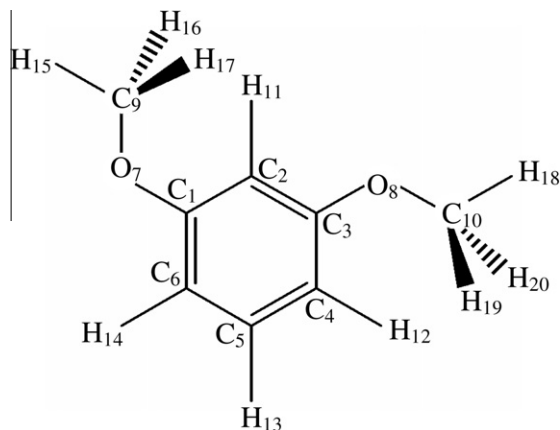
Fig. 1. Most stable conformer of 1,3-DMB with atom numbering.

Fig. 3. Calculated (MP2/6-31G(d)) energy surface in kcal/mol as a function of the two torsional angles around the $C(sp^2)$–O bonds. Three minima occur for $\varphi_1/\varphi_2 = 0°/180°$, $180°/180°$, and $0°/0°$.

respectively (Fig. 2). The geometries of these conformers were fully optimized at the B3LYP and MP2 level of theory with 6-31G(d) and cc-pVTZ basis sets. The vibrational frequencies were calculated by all methods with the exception of MP2/cc-pVTZ. All calculations were performed with the Gaussian03 program package [11].

The *syn–anti* conformer is the global minimum according to all calculations, whereas the *anti–anti* and *syn–syn* structures are higher in energy by about 0.4 and 0.6 kcal/mol. The mole fractions of these conformers were estimated from the theoretical relative Gibbs free energies (Table 1). All methods predict practically the same conformational composition of 1,3-DMB. The results of B3LYP and MP2 geometry optimization with cc-pVTZ basis set for all conformers together with the final experimental GED results are listed in Tables 2–4.
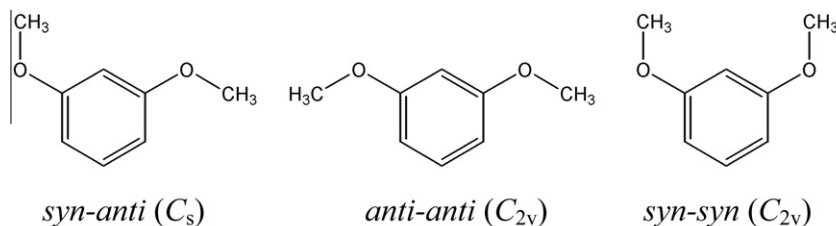
3. Electron diffraction analysis

3.1. Experimental

A commercial sample of 1,3-DMB with purity of 99% was obtained from Aldrich Chemical Co. and used without further purification. Electron diffraction intensities were recorded using the electron diffraction apparatus at Lomonosov Moscow State University. Information about the experimental conditions for all data sets used in the present investigation is given in Table 5. The wavelength of electrons was calibrated with CCl_4 scattering patterns. The optical densities were measured using an EPSON PERFECTION

Fig. 2. Planar conformers of 1,3-DMB.

Table 1
Equilibrium distribution of 1,3-DMB conformers at 344 K predicted from quantum chemical calculations.[a]

Method	Conformer (symmetry)	φ_1	φ_2	ΔE_0	S_{344}	ΔG_{344}	p_{344}
B3LYP/6-31G(d)	*syn–anti* (C_s)	0	180	0.0	101.6	0.0	66
	anti–anti (C_{2v})	180	180	0.4	100.3	0.9	18
	syn–syn (C_{2v})	0	0	0.6	100.4	1.0	16
B3LYP/cc-pVTZ	*syn–anti* (C_s)	0	180	0.0	101.5	0.0	65
	anti–anti (C_{2v})	180	180	0.4	100.3	0.8	20
	syn–syn (C_{2v})	0	0	0.6	100.5	1.0	15
MP2/6-31G(d)	*syn–anti* (C_s)	0	180	0.0	103.6	0.0	67
	anti–anti (C_{2v})	180	180	0.5	102.6	0.9	18
	syn–syn (C_{2v})	0	0	0.7	102.6	1.0	15
MP2/cc-pVTZ[b]	*syn–anti* (C_s)	0	180	0.0	103.6	0.0	64
	anti–anti (C_{2v})	180	180	0.4	102.6	0.7	21
	syn–syn (C_{2v})	0	0	0.6	102.6	1.0	15

[a] Torsional angles φ_1 and φ_2 in degrees; $E_0 = E_e + ZPE$ (in kcal/mol), where E_e is the electronic energy, ZPE is the zero point energy correction calculated from scaled vibrational frequencies; S_{344} (in cal/(K mol)) is the entropy value at 344 K calculated using scaled frequencies; $\Delta G_T(i) \approx \Delta E_0(i) + T \Delta S_T(i)$ is the free Gibbs energy (kcal/mol); $p_T(i) = [\exp(-\Delta G_T(i)/RT)]/[\sum_i[\exp(-\Delta G_T(i)/RT)]$ is the mole fraction of conformers (%).
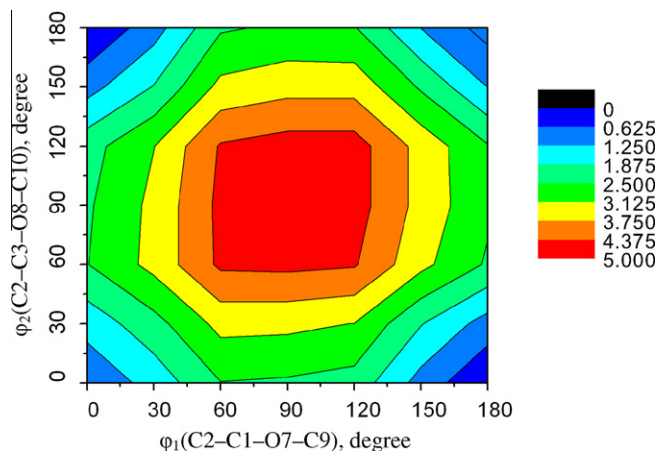[b] ZPE and vibrational frequencies from MP2/6-31G(d) calculation are used.