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Effect of Anisotropy on the Chemical Shift of Vinyl Protons in *trans*- and *cis*-1,2-Dibenzoylethylenes

A Small-Group or Recitation Activity

Roosevelt Shaw,* David Roane, and Sean Nedd

Department of Chemistry, Morgan State University, Baltimore, MD 21251; *rshaw@moac.morgan.edu

The photochemical conversion of *trans*-1,2-dibenzoyl-ethylene (*trans*-1,4-diphenyl-2-butene-1,4-dione) (**1**) to the *cis* isomer (**2**) and thermal reconversion of **2** to **1** are the basis of a hands-on and mind-alert activity for undergraduate organic chemistry students (see Fig. 1). The chemistry of this isomeric conversion was discovered in 1902 (1), suggested as an undergraduate experiment in 1973 (2), and currently is presented as a feasible microscale laboratory exercise (3).

Now, the enhanced pedagogical value of interpreting the ^1H NMR spectra of this alkene diastereomeric pair and several others is being realized in small group settings. For instance, ref 3 lists the δ values of the ^1H NMR signals of **1** and **2**. (The spectra were run in chloroform-*d*, δ 7.26 on a 300-MHz spectrometer.) The spectrum of each isomer contains only one singlet (except for the one due to chloroform), which must represent the vinyl protons. This is at δ 8.01 for **1** and at δ 7.14 for **2**.

Combining molecular modeling and model-building with diamagnetic anisotropy, students are able to provide a plausible explanation for this pronounced chemical shift difference and for chemical shift differences for vinyl protons in other alkene diastereomeric pairs. This paper describes a simple classroom activity students can use to aid them in explaining chemical shift differences for vinyl protons in alkene diastereomers.

The Activity

Working in groups of two, students first build a computer model of **1** in PC Spartan Plus version 2.0.¹ Second, they request a series of calculations to obtain the best stable conformer for **1** as shown in Figure 1. They start with an MMFF molecular mechanics model² to produce the best conformer, follow this by an AM1 semiempirical calculation to establish the equilibrium geometry of this conformer, and end with a single ab initio 6-31G(*) Hartree–Fock calculation

Table 1. Dihedral Angles in Stable Conformers of 1,2-Dibenzoylethylenes

Dihedral Angle	θ (Absolute Value)	
	Trans Isomer	Cis Isomer
O1–C1–C2–H2	147.47°	86.56°
O1–C1–C2–C3	32.04°	91.96°
H3–C3–C4–O4	147.47°	86.56°
O4–C4–C3–C2	32.04°	91.96°
C6–C5–C1–C2	22.53°	31.21°
C8–C7–C4–C3	22.53°	31.21°

Table 2. Intramolecular Distances in Stable Conformers of 1,2-Dibenzoylethylenes

Atoms	Intramolecular Distance/nm	
	Trans Isomer	Cis Isomer
H2–O4	27.17	42.59
H3–O1	27.17	42.59
H2–C5	27.16	30.59
H3–C7	27.16	30.59

to obtain the lowest energy of this conformer (4). Next, they measure dihedral angles (Table 1) and intramolecular distances (Table 2) in this stable conformation of **1** (4). They now build a computer model of **2** and repeat the same procedure to obtain the best stable conformer for **2** (Fig. 1). They also measure the same dihedral angles (Table 1) and intramolecular distances (Table 2) in this stable conformation.

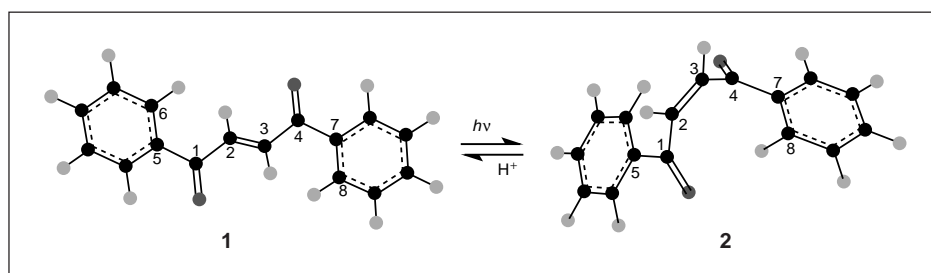


Figure 1. Forward reaction: Photochemical conversion of *trans*-1,2-dibenzoyl-ethylene (**1**); reverse reaction: thermal reconversion of *cis*-1,2-dibenzoyl-ethylene (**2**).

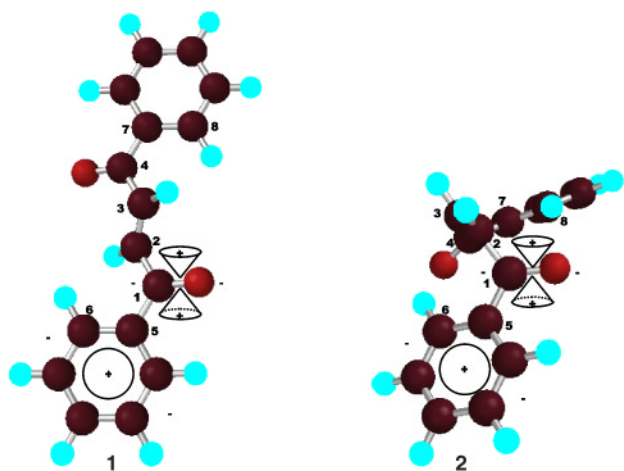


Figure 2. Shielding (+) and deshielding (–) zones associated with the anisotropy of the carbonyl bond and the benzene ring in *trans*-1,2-dibenzoyl ethylene (**1**) and *cis*-1,2-dibenzoyl ethylene (**2**).

Finally, students build reasonably accurate ball-and-stick models of the computer-drawn conformations of **1** and **2** to see better and appreciate more fully, in a tangible way, these molecular geometries and intramolecular distances. They see that these stable conformations of **1** and **2** are both symmetrical so far as molecular geometries and intramolecular distances are concerned. They also are convinced that the chemical shift difference between the vinyl protons in **1** and **2** cannot be explained by diamagnetic shielding effects (inductive effects and resonance effects).

Students now construct a cone from filter paper (ca. 10 cm in diameter), using a paper clip to hold the cone together. By positioning the cone near a carbonyl group in the models as shown in Figure 2, they can clearly envision two different magnetic field zones. Also, by placing a piece of filter paper, unfolded, above the center of a phenyl group in the models, also shown in Figure 2, they again can clearly envision two different magnetic zones.

Discussion

A plausible explanation for this pronounced chemical shift difference between **1** and **2** clearly involves the overriding effect of the diamagnetic anisotropy of the carbonyl group (5).³ Two cones with their apices at the center of the carbonyl group comprise the shielding (+) zone. The rest of space is the deshielding (–) zone (see Fig. 2). Each vinyl proton is, of course, deshielded by the carbon–carbon double bond (5) and the carbonyl group directly attached to its carbon. For example, the proton at C2 is deshielded by the C1 carbonyl group. These deshieldings occur in both the *cis* and *trans* isomers. However, in **1**, the protons at C2 and C3 are further deshielded by the carbonyl groups at C4 and C1, respectively. These protons are found to be at a distance of ca. 27.17 nm from the oxygen atoms of the carbonyl groups. Also in **1**, because of the proximity of the protons at C2 and C3 to the ring current effects in the nearby phenyl groups at C1 and C4, respectively, these protons are further deshielded (6).

The intramolecular distance between the proton at C2 and the benzene ring or phenyl group at C1 is ca. 27.16 nm, which is the same distance between the proton at C3 and its nearby phenyl group. This distance is roughly less than the distance between the *cis* vinyl proton and the phenyl group in styrene (ca. 27.92 nm).⁴ The *cis* vinyl proton in styrene is clearly in the deshielding (–) zone of the phenyl group with a δ 5.82 (7). Hence, the vinyl protons at C2 and C3 in **1** are in both the deshielding (–) zones of both carbonyl groups and the nearby phenyl group closer to them. By examining the computer-drawn and then the ball-and-stick models of **2**, it is clear that now these deshieldings are much smaller or nonexistent, since the protons at C2 and C3 are found farther away from the carbonyl groups at C4 and C1, respectively, (ca. 42.59 nm). Also in **2**, the protons at C2 and C3 are found ca. 30.59 nm from their nearby phenyl groups at C1 and C4, respectively. This is well beyond the distance of ca. 27.92 nm between the *cis* vinyl proton and the phenyl group in the styrene but shorter than the distance of ca. 34.75 nm between the *trans* vinyl proton and the phenyl group in styrene.⁴ The *trans* vinyl proton in styrene resonates at δ 5.31 and thus is deshielded only by the carbon–carbon double bond attached to it (7).

Conclusion

This classroom activity introduces students to molecular modeling, improves their model-building skills, and shows them that molecular modeling and model-building can enable them to see ideas more clearly and retain them longer. Moreover, it gives them an excellent feel for the important concept of diamagnetic anisotropy and gives them an opportunity to reach sound conclusions from combining experimental data (NMR) and theoretical data (molecular modeling) using co-operative learning strategies.⁵

Acknowledgments

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Notes

1. The PC Spartan Plus computer software can be purchased from Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612. PC Spartan Plus calculations can be performed quickly on an 800-MHz Pentium III PC running Windows 98 or on other compatible PCs, with clear instructions to the students (see ref 4).

2. Several commercial organic molecular model sets can be used for compound building. In this activity, the Allyn and Bacon set, available from Fisher Scientific, was used.

3. Diamagnetic anisotropy effects are defined as the shielding and deshielding of protons in π -electron systems resulting from the orientation of these systems with respect to an external or applied magnetic field. The circulating π electrons near the protons in such systems create an induced magnetic field that both opposes and augments (reinforces) the applied magnetic field in different magnetic

zones. The zone where opposition to the applied magnetic field occurs is the shielding (+) zone. Protons located in this (+) zone are shielded. They resonate at lower δ values. Their chemical shifts are found farther upfield toward tetramethylsilane (TMS) than electronegativity and resonance would predict. Protons located in the zone of augmentation or reinforcement are in the deshielded (–) zone and thus are deshielded. They resonate at higher δ values. Their chemical shifts are found farther downfield from TMS than electronegativity and resonance would predict as is the case for the vinyl protons in **1**. A detailed explanation of this topic can be found in any modern organic chemistry textbook.

4. To reinforce the concept of diamagnetic anisotropy and to sharpen computer-drawing and model-building skills, students are encouraged to perform the following homework/out-of-class activity. In a designated location equipped with reference materials and computers, student groups first look up the structures of and chemical shifts for the vinyl protons in the following alkenes and alkene diastereomeric pairs: styrene (7), 2,5-dimethylenecyclohexanone (8), fumaric acid and maleic acid (9), and *trans*- and *cis*-stilbene (10). They then build computer drawings and ball-and-stick models of the best stable conformations of these six molecules. Last, they calculate the chemical shifts for the vinyl protons in these molecules (11). Comparisons are made between the reported and calculated values and large deviations (greater than 0.15) are discussed.

5. As demonstrated on a questionnaire, 36 students (97%)

found this activity extremely helpful in understanding the concept of diamagnetic anisotropy. All (100%) indicated that this was their first exposure to molecular modeling.

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