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# Determination of the configuration of a trisubstituted ethene by experimental and theoretical methods

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## Abstract

We report on various attempts to determine the configuration of the double bond of a trisubstituted ethene and demonstrate that ab initio calculations of NMR related properties such as nuclear magnetic shielding constants, are a valuable alternative when experimental methods fail. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* configuration; isomers; thiophenes; quantum-chemical calculations.

## 1. Introduction

Recently we discussed the synthesis and isomerization of 1-cyano-1-(2-thienyl)-2-(3-methoxy-2-thienyl)ethene (abbreviated CTMTE, Fig. 1) and identified the *Z*- and *E*-isomers of this trisubstituted ethene from combined results of ab initio calculations and UV–vis spectroscopy.[1] The calculations indicated that the *Z*-configuration occurred in a non-planar conformation (designated *Z*[*sp*,*ort*]). The twisting of one thiophene ring out of the molecular plane (Fig. 1) reduces the conjugation length, from which we assigned the *Z*-configuration to the compound with the lower $\lambda_{max}$, and hence the *E*-configuration to the compound with the higher $\lambda_{max}$. Although this is a strong indication we wanted to obtain supporting evidence.

In general the configuration at the double bond of a disubstituted ethene can be easily determined by IR from the stretching and bending frequencies and by NMR from the coupling constants $^3J(HH)$ of the CH=CH moiety. However, in the case of trisubstituted ethenes neither simple IR nor NMR data are available to distinguish unequivocally between *E* and *Z*.

Single crystal X-ray diffraction is the most straightforward method to determine the configuration at a double bond as part of the entire geometry. The preparation of a single crystal of *E*-CTMTE failed

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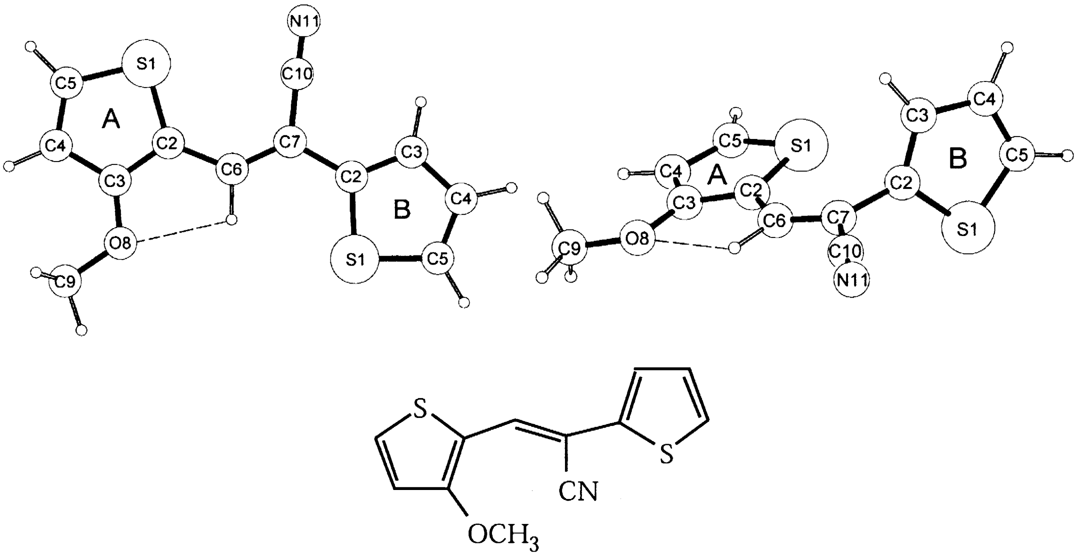

Fig. 1. Atomic numbering of *E*[*sp*,*sp*]-CTMTE (left) and *Z*[*sp*,*ort*]-CTMTE (right). CTMTE: 1-cyano-1-(2-thienyl)-2-(3-methoxy-2-thienyl)ethene

because of the extreme sensitivity of the compound to light. In daylight, a solution quickly converts to an equilibrium mixture of 97% *Z*- and 3% *E*-isomer, and the presence of the latter prevented the crystallization of *Z*-CTMTE.

Next, we considered an indirect method to construct derivatives in which the configuration at the double bond is retained and which crystallize better than the original compounds. We hoped to perform a Diels–Alder condensation on CTMTE, in which *E*-CTMTE would produce a norbornene derivative with one thiophene ring *endo* and one *exo*, while *Z*-CTMTE would yield a norbornene with both thiophene rings either *endo* or *exo*. Unfortunately, however, we did not succeed.

The geometrical differences between both isomers being quite prominent, especially in the vicinity of the B-ring, then led us to attempt nuclear Overhauser effect (NOE) NMR spectroscopy to assign the configuration of the double bond by exploiting the difference in interatomic distances between the vinylic proton H(6) and the aromatic proton H(3B). However, this procedure was also unsuccessful.

Finally, we turned our attention to theoretical chemistry. It has been shown that the calculation of NMR coupling constants and chemical shifts by ab initio methods is a significant addition to the chemists' tools in assigning spectra.[2–5] To test the scope further, we computed the nuclear magnetic shielding factors, $\sigma$, of the carbon atoms in *E* and *Z*[*sp*,*ort*]-CTMTE. We report here that these calculations provided decisive evidence for the configurational assignments.

### *1.1. Computational methods*

The atomic numbering of the compounds is given in Fig. 1. The ab initio calculations were performed as is described previously by us.[1] Shielding constant calculations were performed using the program TEXAS93,[6] applying the GIAO method, on both the *E*- and *Z*[*sp*,*ort*]-form of CTMTE in their refined geometries. Since experimental chemical shifts $\delta$ in solution are compared to theoretical values, only the averaged shielding constants $\sigma$ were used. The values of the carbon atoms in CTMTE are listed in Table 1 for both isomers.

Table 1
Experimental chemical shifts $\delta$ of the carbon atoms in both isomers ($\delta$ in ppm relative to TMS, solvent $(CD_3)_2CO$), together with the difference $\Delta\delta=\delta$(isomer 1)–$\delta$(isomer 2). Theoretical nuclear shielding factors $\sigma$ of the carbon atoms in both isomers, together with the difference $\Delta\sigma=\sigma(Z)-\sigma(E)$ (for atomic numbering, see Fig. 1)

| | $\delta$(isomer 1) | $\delta$(isomer 2) | $\Delta\delta$ | $\Delta\sigma$ | $\sigma(Z)$ | $\sigma(E)$ |
|---|---|---|---|---|---|---|
| **C(2A)** | 115.0 | 114.1 | 0.9 | 1.2 | 90.7 | 89.5 |
| **C(3A)** | 161.6 | 161.9 | -0.3 | -0.1 | 45.3 | 45.4 |
| **C(4A)** | 115.7 | 115.0 | 0.7 | 0.1 | 92.1 | 92.0 |
| **C(5A)** | 130.0 | 129.0 | 1.0 | -0.6 | 59.8 | 60.4 |
| **C(2B)** | 139.5 | 133.3 | 6.2 | 7.5 | 64.9 | 57.4 |
| **C(3B)** | 125.4 | 129.8 | -4.4 | -5.8 | 73.4 | 79.2 |
| **C(4B)** | 128.2 | 128.0 | 0.2 | 1.4 | 79.1 | 77.7 |
| **C(5B)** | 125.7 | 131.8 | -6.1 | -7.4 | 67.5 | 74.9 |
| **$CH_3O$-** | 58.7 | 58.6 | 0.1 | 0.0 | 151.8 | 151.8 |
| **-CH=** | 129.1 | 136.1 | -7.0 | -9.7 | 59.6 | 69.3 |
| **$\underline{\text{C}}$CN** | 98.4 | 97.6 | 0.8 | 2.0 | 106.2 | 104.2 |
| **CN** | 117.2 | 119.6 | -2.4 | -3.8 | 91.9 | 95.7 |

## 2. Results and discussion

### 2.1. Diels–Alder reaction

The presence of the nitrile group on the double bond in CTMTE suggested that the compound could be used as a dienophile in a Diels–Alder condensation with a diene, like furan. In fact, the ab initio calculations had indicated that the bond length of C(6)–C(7) is indeed larger than in similar compounds lacking the nitrile group, suggesting that CTMTE might be activated for this type of condensation. However, upon refluxing the compound in its *Z*-form with an excess of furan in methanol for an extended period of time no trace of any condensation product could be found.

### 2.2. Experimental NMR

Due to the position of the *Z*/*E* equilibrium at 97% *Z*/3% *E*, separate spectra of both isomers could be easily recorded. The $^1$H-spectra of both isomers were easily assigned using known coupling patterns and constants of the thiophene protons; a small homoallylic coupling ($^5$J=0.5 Hz) between the vinylic hydrogen atom H(6) and H(5A) was found, which has never been reported in similar compounds. Due to the unsymmetrical nature of CTMTE the $^{13}$C-spectrum was not straightforward. However, using short and long range 2D-techniques the signals in both isomers' spectra were unequivocally assigned. Nevertheless, the simple 1D-spectra of the pure compounds do not give any indication about the configuration of the double bond.

### *2.3. NOE-experiment*

To prove the structure of the two isomers of CTMTE, a NOE-difference experiment was carried out on both. Based on the ab initio calculations, the distance between the vinylic proton H(6) and the aromatic proton H(3B) in the *Z*-isomer is 4.367 Å, while for the *E*-isomer a value of 4.662 Å was calculated. This is within the theoretical range for a NOE-effect to be seen.[7] Moreover, because of the difference in distance we hoped that a more pronounced NOE-effect could be detected for the *Z*-isomer. Unfortunately, irradiation of the vinylic proton H(6) in both cases showed no enhancement of any other signal in the proton spectrum, which means that no information could be obtained with regard to the structure of the two isomers in hand.

### *2.4. Shielding factor calculations*

Since the chemical shift $\delta$ is inversely proportional to the shielding factor $\sigma$, a large nuclear shielding corresponds to a small chemical shift. The differences are quasi-independent of the surroundings of the molecule and can be used to compare experiment and theory: both the magnitude and the sign of the difference for a certain carbon atom obtained in the calculations must correspond to the same values in the experimental spectrum. Since the configurations of the calculated geometries of both most stable isomers are absolute, this procedure will unequivocally produce the configurations of the isomers in solution. Table 1 lists the experimental chemical shifts of both isomers (here referred to as isomer 1 and isomer 2, i.e. without any previous assignment) and the corresponding difference $\Delta\delta$; it also lists the theoretical shielding factors of both isomers (here with the known configuration) and the corresponding difference $\Delta\sigma$. From Table 1 it is obvious that the values of $\Delta\sigma$ correspond with the values of $\Delta\delta$ and, since $\Delta\sigma=\sigma(Z)-\sigma(E)$ and remembering that $\Delta\delta=-\Delta\sigma$, isomer **1** must be *E*-CTMTE and isomer **2** must be *Z*-CTMTE, completely in line with the results from the UV–vis analysis.

## 3. Conclusions

No experimental technique was able to provide us with direct evidence of the configuration of the trisubstituted double bond in CTMTE. Only when complemented with the results of ab initio calculations do they enable us to assign a configuration to the separate isomers. Furthermore, we must emphasize the extraordinary match that exists between the values of $\Delta\sigma$ and $\Delta\delta$. This proves the important role ab initio calculations can play to support experimentalists in their analysis of spectroscopic data and even more so when experimental methods fail to produce an adequate explanation or assignment.

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