

## Bond Order Calculations on Neutral Molecules and Radical Cations: Predicting Fragmentation Patterns of $\alpha$ -Phenylcinnamic Acid Silylesters on Electron Impact Ionization

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### Introduction

The Perkin condensation of benzaldehyde and phenylacetic acid in the presence of triethylamine gives an isomeric mixture of  $\alpha$ -phenylcinnamic acids (1). The isomeric ratio can be influenced by the solvent, reaction time, temperature of reaction, etc. The composition can be accurately determined by GC-MS measurements after derivatization: through the analysis of the trimethylsilyl or the *t*-butyldimethylsilyl derivatives of the acids (2).

Upon EI (electron impact) ionization several secondary transformations proceed in the mass spectrometer, such as fragmentation and rearrangement reactions. Principally, the basic cleavage pattern can be predicted by bond order calculations. Bond orders can be computed e.g., after full geometric optimization of the positively charged radicals (parent ions). Any well-parametrized force field, semiempirical or *ab initio* methods should be able to simulate the actual events well, since ions in the mass spectrometer can be taken as isolated (gas phase, very low concentration). In this paper results of this nature and predictions based on them are reported.

### Methods

The *E* and *Z* isomers of the trimethylsilyl esters of  $\alpha$ -phenylcinnamic acids (the neutral molecules, Fig. 1) and their radical ions were fully optimized with the AM1 (3) semiempirical method included in the PcMol 3.1 package (4).

After optimization, bond orders, which were taken as a measure of bond strength, were computed.

### Results and Discussion

The standard enthalpies of formation for the neutral molecules were close to each other ( $\Delta H_E = -320.7$  kJ/mol,  $\Delta H_Z = -319.2$  kJ/mol) as were those of the radical cations ( $\Delta H_E = 647.7$  kJ/mol,  $\Delta H_Z = 650.2$  kJ/mol).

The results of bond order calculations on the neutral molecules as well as on the radical cations are summarized in Table 1.

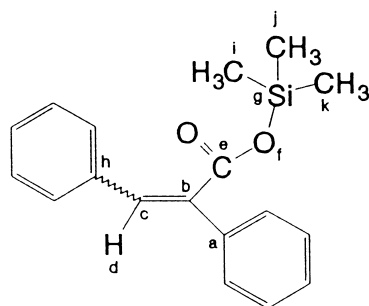


FIG. 1. The structural formulae of  $\alpha$ -phenylcinnamic acid trimethylsilyl ester isomers (**I**).

TABLE I. Bond orders in the parent ions (normal) and the neutral molecules (italics) of trimethylsilyl ester derivatives (two molecules: *E* and *Z* isomers and two radical ions: *E* and *Z* isomers) of  $\alpha$ -phenylcinnamic acid isomers (**I**, see Fig. 1) determined for geometries optimized by AM1 semiempirical quantum chemical method.

Bonds	<b>I</b>			
	<i>E</i>		<i>Z</i>	
a-b	1.14	<i>0.99</i>	1.15	<i>0.99</i>
b-c	1.45	<i>1.82</i>	1.44	<i>1.84</i>
b-e	0.94	<i>0.94</i>	0.94	<i>0.92</i>
c-d	0.93	<i>0.94</i>	0.93	<i>0.94</i>
c-h	1.20	<i>1.02</i>	1.20	<i>1.02</i>
e-f	1.04	<i>1.12</i>	1.04	<i>1.11</i>
f-g	0.67	<i>0.65</i>	0.67	<i>0.65</i>
g-i	0.88	<i>0.87</i>	0.89	<i>0.87</i>
g-j	0.88	<i>0.88</i>	0.88	<i>0.88</i>
g-k	0.91	<i>0.88</i>	0.91	<i>0.88</i>

It should be noted that some bonds became significantly weaker in the parent ion than they were in the neutral molecules (C=C double bonds, C-O ester bonds). The C(double bonded carbon)-C(phenyl carbon) bonds became stronger, while the others did not change. Over all, the O-Si bond was found to be the weakest. The Si-C and ester groups also have bond orders smaller than one. It is also clear that there was no significant difference in bond strength between the two isomers.

Based on these observations and the specific numerical values, some predictions can be made: i) the fragmentation pattern for the two isomers should not differ significantly; ii) the most abundant fragment ought to form via the rupture of the O-Si bond; iii) the rupture of the C(double bonded carbon)-C(silylester) and the Si-C bonds ought to be facile; iv) the second bond of the C=C double bond should break relatively easily; v) C(double bonded carbon)-C(phenyl carbon) bonds should be less susceptible to cleavage.

The validity of the above predictions was verified experimentally (Table 2).

TABLE 2. Most abundant fragments, their  $m/z$  values and relative intensities in the EI mass spectra of *E*- and *Z*- $\alpha$ -phenylcin-namic acid trimethylsilyl ester isomers (structure 1 in Fig. 1;  $M^+$  stands for the parent ion, of the whole molecule;  $m/z$  is the mass/charge ratio).

Fragments	$m/z$	Relative intensities/%	
		<i>E</i>	<i>Z</i>
$M^+$	296	78.2	48.6
$[M - CH_3]^+$	281	64.1	43.2
$[C_{16}H_{17}Si]^+$	237	11.5	8.1
$[M - OSi(CH_3)_3]^+$	207	16.7	9.5
$[M - CO_2Si(CH_3)_2]^+$	179	100.0	100.0
$[M - H - CO_2Si(CH_3)_3]^+$	178	82.1	81.1
$[C_8H_{12}OSi]^+$	152	15.4	12.2
$[C_3H_{11}Si]^+$	135	20.5	21.6
$[(CH_3)_3SiO]^+$	89	5.1	8.1
$[(CH_3)_2SiOH]^+$	75	19.2	24.3
$[(CH_3)_3Si]^+$	73	70.5	100.0
$[SiOH]^+$	45	20.5	33.8

### Acknowledgements

This work was sponsored by the National Science Foundation of Hungary through grant F4297/1992. B.T. acknowledges the Research Fellowship given to him by the Foundation for Hungarian Science, their invaluable help was highly appreciated.

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