Studies of NMR Chemical Shifts of Chalcone Derivatives of Fivemembered Monoheterocycles and Determination of Aromaticity Indices

Eun Jeong Jeong and In-Sook Han Lee*

Department of Science Education, Kangwon National University, Chuncheon 24341, South Korea. *E-mail: ishl@kangwon.ac.kr Received March 1, 2019, Accepted April 12, 2019

A series of the chalcone derivatives of the five-membered monoheterocyclic compounds, (*E*)-1-aryl-3-heteroarylpropen-1-ones, were prepared by aldol condensation of the corresponding aldehydes of thiophene, pyrrole, and furan with *m*- and *p*-substituted acetophenones. Similar condensation of the acetyl compounds of the heterocycles with *m*- and *p*-substituted benzaldehydes gave another series of the chalcone derivatives, (*E*)-1-heteroaryl-3-arylpropen-1-ones. The ¹³C chemical shift values (δ_C) of the chalcone derivatives were determined in order to find if they correlated with the Hammett σ values. A good correlation, especially for the β -C for both series, was found for the ¹³C chemical shift values (δ_C) of the chalcone derivatives with the Hammett σ values. The chemical shift values of the β -C of the heterocyclic compounds were plotted against those of the benzene derivatives. The resulting slopes were found to be close to the values of the aromaticity indices.

Keywords: Heterocyclic compounds, Indices of aromaticity, Hammett equation

Introduction

One of the most important concepts in organic chemistry is aromaticity. The term "aromaticity" is quite conveniently used in explaining the physical and chemical behavior of many cyclic compounds. It is not surprising to find countless research articles related to the aromaticity.¹ The concept of aromaticity was originally coined to explain the unique nature of benzene and its derivatives. Many organic chemistry textbooks cover the concept by listing a few criteria for the aromaticity²: (1) cyclic compound with a large resonance energy, (2) tendency to react by substitution rather than addition, (3) (4n + 2) electrons in a ring, and (4) ability to support a diamagnetic ring current.

The concept of aromaticity has been expanded to the non-benzenoid compounds such as five-membered monoheteroaromatic cyclic compounds like thiophene, pyrrole, and furan. Naturally, many attempts have been made for the quantification of the relative aromaticity of the heterocycles.³ A quantitative measure of aromaticity may include two experimental methods. One is to measure the energy (e.g., heat of formation) of the compound in question and to compare this with that of a hypothetical model compound without the cyclic conjugation.⁴ Another is to look in particular at the geometries and magnetic properties of aromatic compounds and then compare them with non-aromatic analogs.⁵ In addition to the experimental methods molecular orbital calculation is widely carried out to come up with a better understandings about the aromaticity.⁶ Table 1 lists the aromaticity indices frequently cited in literatures, which should be directly related to the current paper.

Generally speaking, Table 1 shows the indices of aromaticity decreasing from benzene, thiophene, pyrrole, and to furan. Although the numerical values for the indices were not given, a similar order of the decrease was reported by the measurement of ${}^{1}J_{(CC)}$ spin–spin coupling constants for the five-membered heterocycles.¹⁴

Whatever method is employed, there seems to be problems in the quantitative aromaticity scale. The problems are encountered because of (1) the difference between the electronic structure of the heteroatom and carbon, (2) incompatibility of the different physical and chemical molecular characteristics, (3) comparison of the experimental data obtained in different media, and (4) difficulties in the definition of the non-aromatic model to compare with the aromatic compound.

NMR spectroscopy has been employed as a tool for the determination of the aromaticity.¹⁵ Typically, ring-current intensity and nucleus-independent chemical shifts are the criteria for the aromaticity. On the other hand, the comparison of the chemical shift values of one series of aromatic compounds to those of another series may be used as a measure of the relative aromaticities of the two aromatic rings.

There are several reports on the values of the indices of aromaticity for the five-membered monoheterocyclic compounds using NMR spectroscopy in this way.¹⁶ At first, the chemical shift values of *m*- and *p*-substituted

					-
Table 1.	Values	of aroma	ticity in	dices ir	literatures.

Method	Benzene	Thiophene	Pyrrole	Furan
Ring current ⁸	1.00	0.75	0.59	0.46
Bond length ⁹	1.00	0.93	0.91	0.87
Dewar resonance energy ¹⁰	22.6	6.5	5.3	4.3
Hess–Schaad resonance energy ¹¹	9.0	4.5	5.3	1.0
E_{TRPE}^{12}	45.7	33.0	40.0	7.0
$I_{\rm NG}^{12}$	40.9	39.5	38.7	36.7
I _{ring} 5b	0.0883	0.0696	0.0962	0.0541
R _{CI} 5b	1.751	1.450	1.464	1.431
I _A 5b	100	81.5	85	5.3
Dilution shift method ¹³	13.93	11.56	_	7.67

benzophenones were compared with the aryl ketones of the heterocycles.16a Similar approaches were made with the substituted phenyl esters16b, c and amides.16d

The present paper reports the values of the indices derived from the values of the chemical shifts of the two chalcone series, (E)-1-aryl-3-heteroarylpropen-1-ones (1–4) and (E)-1-heteroaryl-3-arylpropen-1-ones (5–8).

Experimental

(NMR) Nuclear magnetic resonance spectra in chloroform-d solution were recorded on a Bruker DPX-400 FT NMR spectrometer (Billerica, MA, USA) in the Central Lab of Kangwon National University at 400 MHz for ¹H and 100 MHz for ¹³C and were referenced to tetramethylsilane. The solutions were 0.10 M in CDCl₃. Each solution was prepared in a 1 mL cylindrical volumetric flask by weighing the compound into the flask and filling with the solvent containing 1%-TMS. A portion (0.60 mL) of the solution was transferred into a 5 mm NMR tube and the spectrum was obtained at 20°C. The σ values for the *m*and p-substituents are from the literature.¹⁷

Benzaldehyde, 2- and 3-thiophenecarbaldehydes, 2-pyrrolecarbaldehyde, 2- and 3-furfurals, and *m*- and *p*substituted acetophenones were the commercial products and used as delivered. Column chromatography was performed using silica gel and a 1:1 mixture of ethyl acetate and hexane as the elution solvent. The chalcone derivatives were prepared by following the procedures reported.^{14,18,19} Yields are listed in the supporting information. ¹H and ¹³C NMR spectral data are also listed in the supporting information.

Preparation of the Chalcones. An Illustrative Procedure with (*E*)-1-Aryl-3-(2-pyrrolyl)-2-propenones (3k). 2-Pyrrolecarbaldehyde (12 mmol), acetophenone (13 mmol), and 24 mmol of NaOH in ethanol (20 mL) and water (10 mL) were mixed in an ice-bath and stirred for 4 h in the bath. The mixture was neutralized with 1 M-HCl aqueous solution to pH 8–9. The resulting precipitate was collected and recrystallized from ethanol.

Results and Discussion

Chalcones are widely known compounds and their syntheses are extensively reported. In addition, chalcone has a structural characteristic of α,β -unsaturated carbonyl skeleton, which raises various spectroscopic interests. The presence of an enone moiety in chalcone has been the point of interest in studying the transmission of the electronic effect of the substituent from one aryl ring to the other ring. For example, the carbonyl stretching frequencies in 1-phenyl-3-(5-aryl-2-furyl or 2-thienyl)propenones were studied in order to compare the effect of the heterocyclic rings in the transmission of the electronic effect.²⁰ (*E*)-1-(5-methyl-2-furyl)-3-(substituted phenyl)-2-propen-1-ones (8, 5-CH₃) were synthesized by crossed-aldol condensation between 2-acetyl-5-methylfuran and substituted benzaldehydes.²¹ The ¹H and ¹³C chemical shift values were attempted to correlate with the Hammett substituent constants to show poor correlation coefficients. The antimicrobial activities were also examined.

At first we were interested in preparing chalcone derivatives of five-membered monoheterocyclic compounds in order to evaluate various biological activities. We attempted to prepare the chalcone derivatives according to the Scheme 1.

Aldol condensation between benzaldehyde and acetophenones were very effective, giving the chalcones, (E)-1-aryl-3-phenyl-2-propenones (1) in over 90% yields.²² Similarly, (E)-1-phenyl-3-aryl-2-propenones (5) were prepared from the condensation of acetophenone with m- and p-substituted benzaldehydes in good yields. (E)-1-Aryl-3-(2-thienyl)-2-propenones (2) were prepared by the aldol condensations of 2-thiophenecarbaldehyde with m- and psubstituted acetophenones in the presence of NaOH in ethanol-water solution.²³ Condensation of 2-acetylthiophene with the substituted benzaldehydes gave 6. The yields of 2 and 6 were generally good (60-90%).¹⁸ Series of (E)-1-aryl-3-(2-pyrrolyl)-2-propenones (3), that were aldol condensation products between pyrrole-2-carbaldehyde and m-



Z: a, m-NO₂; b, m-Br; c, m-Cl; d, m-OCH₃; e, m-CH₃,

f, p-NO₂; g, p-Br; h, p-Cl; i, p-OCH₃; j, p-CH₃, k, H

Scheme 1. Synthesis of the Chalcone Derivatives.

and *p*-substituted acetophenones, were prepared,¹⁹ but the yields were not as good as the thiophene series. On the other hand, the yields of **7** which were the condensation products of 2-acetylpyrrole with *m*- and *p*-substituted benzaldehydes were good (75–91%) under similar reaction conditions. Similarly, the condensation of furfural with the acetophenones gave the chalcone analogs **4** and the similar reaction of 2-acetylfuran with the substituted benzaldehydes resulted **8** in moderate yields (40–60%).

All the products were purified by recrystallization from ethanol to analytical purity, which is essential for spectroscopic analysis. The NMR spectra of **1–8** were obtained in 0.1 M CDCl₃ solutions. Assignments were made with the aid of ¹H—¹H COSY and ¹H—¹³C HETCOR spectroscopy. The complete chemical shift data are not listed in the present paper because of the limited space and the objective of the current paper is to discussing the aromaticity.

The substituent effect on the chemical shift is typically analyzed by the single substituent parameter (SSP) and dual substituent parameter (DSP) approach, which are represented by Eqs. (1) and (2), respectively.²⁴

$$\delta = \rho \sigma + \delta o \tag{1}$$

$$\delta = \rho_{\rm I} \sigma_{\rm I} + \rho_{\rm R} \sigma_{\rm R} + \delta o \tag{2}$$

Figure 1 shows the correlations of the chemical shift values of the β -Cs of **1–8** with the Hammett σ values¹⁷ according to Eq. (1).

Table 2 lists the slopes (ρ) and the correlation coefficients (*r*) obtained from the similar plotting with the values of the chemical shifts of C=O, α -C, β -C, and *i*-C of **1–8**.

There are several striking characteristics in Table 2. One of them is the negative values of the slopes for the carbonyl and the *ipso*-Cs. Furthermore, the correlations are poor for the carbonyl carbons (r = 0.525-0.597) of **1–4**. The poor correlation for the substituted benzoyl series is not surprising because the substituted benzoyl derivatives show poor correlation similarly for the carbonyl carbon.¹⁶ Solaniova



Figure 1. Correlation between σ and ¹³C chemical shifts of β -carbons in **1–8** in 0.1 *M*-chloroform-*d*.

Table 2. Slopes and correlation coefficients (ppm) of the plots of 13 C chemical shift values against the Hammett σ .

	C=0)	α-C	2	β-C	2	i-C		
	ρ <i>r</i>		ρ	r	ρ	r	ρ	r	
1	-142.66	0.573	-121.42	0.844	268.96	0.994	-91.68	0.997	
2	-148.60	0.597	-144.80	0.878	247.23	0.994	-73.58	0.992	
3	-111.69	0.525	-91.87	0.809	204.68	0.991	-5.92	0.800	
4	-154.61	0.621	-121.19	0.845	204.62	0.994	-57.34	0.993	
5	-109.12	0.967	472.32	0.978	-371.82	0.952	-92.03	0.997	
6	-94.09	0.972	458.33	0.941	-352.47	0.953	-78.40	0.996	
7	-69.97	0.980	356.61	0.859	-290.47	0.937	-9.79	0.822	
8	-56.74	0.992	310.34	0.875	-289.71	0.959	-65.55	0.982	

et al. investigated the substituent effect of chalcones having para substituents in terms of the field (*F*) and resonance (*R*) parameters and reported the directions of the two effects were opposite (-F and +R) for **1** and same (-F and -R) for **5**.²² We reported the positive ρ values for the electron-donating substituents and the negative ρ values for the electron-withdrawing substituents,^{16,18} which resulted in poor correlation overall.

In contrast, the correlations are good (r = 0.967-0.992) for the carbonyl carbon shifts of **5–8**, although the absolute magnitude of the ρ values are smaller (ca. 63–76%) than those of **1–4**. The distance between the substituent and the carbonyl carbon atom is much closer in **1–4** than in **5–8**, which could be the cause of the smaller ρ values (approximately –111.69 to –154.61 ppm for **1–4** vs. –56.74 to –109.12 ppm for **5–8**).

The inverse correlation of the chemical shifts of the carbonyl carbons in **5–8** with good to excellent correlation coefficients may be the result of the alternating π –polarization²⁵ as **I**:



Similar polarization may be operating in 1-4, but the presence of the carbonyl group bonded directly to the phenyl ring having the substituent should affect the electronic effect of the substituent differently depending on the nature of the substituent (electron-donating group *vs.* electron-withdrawing group), as shown in **II** and **III**.

Such a polarization effect should cause the inverse correlations ($\rho = -289.71 \sim -371.82$ ppm) of the chemical shifts of the β -Cs in **5–8**, which are confirmed from Table 2. The inverse correlations observed for the β -Cs in **5–8**, are striking contrasts to the normal correlations ($\rho = 174.82 - 268.96$ ppm) in the cases of **1–4**, as shown in Table 2. The inverse substituent effect was reported for the α -Cs of *m*- and *p*-substituted styrene²⁶ and for the α -Cs of the substituted cinnamate esters.²⁷

The phenomenon of the alternating π polarization is evidenced by the observation of the normal correlation for



Figure 2. Correlation of ¹³C chemical shifts of the β -Cs in the heteroaryl chalcones 2–4 with those in the chalcones 1.

the chemical shifts of the α -Cs ($\rho = 310.34-472.32$ ppm) for **5–8**. A similar correlation was reported for the ¹³C NMR spectra of pyridine chalcone analogs.²⁸

It is worthwhile to point out that the absolute magnitude of the slope is the largest for the β -Cs among **1–4** and α -Cs among **5–8**. The latter is expected because the carbon atom is the β -C of the styryl system (ZC₆H₄CH = ^{*}CH₂).^{26,27} However, the β -C in **1–4** is separated by three bonds from the benzene ring having the substituents at *m*- and *p*-positions, and the through-bond transmission of the electronic effect of the substituent cannot explain the largest values of the slopes. Apparently, the effect may be transmitted through space as shown in **IV**.



When the values of the chemical shifts of the β -Cs in the heterocycles **2–4** are plotted against those in the benzene derivatives **1**, excellent correlations (r = 0.999) were observed as shown in Figure 2. Similar plotting with the heterocycles **6–8** against the benzene derivatives **5** also showed a good correlation. Table 3 lists the slopes and the correlation coefficients of such plots for C=O, α -C, β -C, and *i*-C.

Table 3 clearly reflects that the thiophene ring bonded to the β -C of propenone behaves magnetically very close to benzene ring with slopes of **2**/1 near unity (0.92–1.14)

for C=O, α -C, β -C, and *i*-C with the excellent *r* values (0.992–0.999). When the thiophene ring is bonded to the carbonyl carbon, the values of the slopes of **6/5** for C=O, α -C, and *i*-C decrease about 10%. However, the slope for the β -C shows a slight increase (0.92 for **2/1** to 0.95 for **6/5**).

The correlations of the furan series with the benzene series (4/1 and 8/5) are also excellent (r = 0.990-0.999). It should be pointed out that the slopes of the plots of 2/1 and 4/1 for the carbonyl carbon are same (1.00). Both S and O atoms belong to the group VI in the periodic table and the overall electronic effect may be similar because the hetero atoms and the carbonyl carbon atom are apart by four bonds. Apparently, the chemical shift of the carbonyl carbon atom seems to be influenced mostly by the electronic effect of the substituent and the nature of the aryl group at the β position is not important except the case of pyrroles 3 and 7.

The value of the slope for the carbonyl carbon atom of the pyrrole against the benzene (3/1) is smaller (0.84) than the analogous slope values of thiophene and furan (1.00). The resonance contribution of the N atom should be much more significant than that of S or O atom, as shown in V and VI. The electronic effect of the substituent should be transmitted differently through the extended conjugation of the double bonds, which leads to the smaller value of the slope



The significant contribution of the resonance structures **V** and **VI** in the pyrrole compounds are well reflected by the slopes of near zero for the *ipso* carbon in the plots of **3/1** and **7/5** with the poor correlation coefficient values. Such a resonance contribution should be minimal with the benzene ring or the heterocyclic rings having S and O atoms.

The values of the slopes for the α -Cs are very close also for thiophene (1.14) and furan (1.13). The α -C is separated from the hetero atom by three bonds, and the unshared electron pair orbital should be close to the *p* orbital of the α -C, as shown in **VII**. Therefore, the

Table 3. Slopes and correlation coefficients of the plots of 13 C chemical shift values of the heterocycle series (2–4 and 6–8) *vs.* those of the benzene series (1 and 5).

	2/1 slope	r	3/1 slope	r	4/1 slope	r	6/5 slope	r	7/5 slope	r	8/5 slope	r
C=O	1.00	0.999	0.84	0.982	1.00	0.998	0.86	0.998	0.64	0.965	0.52	0.990
α-C	1.14	0.997	0.75	0.955	1.13	0.993	0.99	0.982	0.71	0.830	0.66	0.983
β-C	0.92	0.999	0.76	0.999	0.76	0.999	0.95	0.999	0.79	0.992	0.76	0.985
i-C	0.94	0.999	0.00	0.035	0.74	0.999	0.86	0.998	0.11	0.865	0.71	0.995

4

susceptibility of the substituent effect may be greater in 2 and 4 than in 1, which leads to the values of the slopes greater than unity.



The most important observation from the values of the slopes in Table 3 is for the β -Cs. The β -C atom is bonded directly to the benzene and the heteroaryl rings. Therefore, the values of the slopes should be considered as a measure of the overall influence of the heteroaryl ring that is compared to the benzene ring. If we define the aromaticity as the overall influence of the benzene ring, the relative magnitude of the slope of a plot for a heteroaryl system against a benzene system many be considered as the index of the aromaticity. Such logic may lead to the values of the slopes 0.92, 0.76, and 0.76 for the β -Cs of **2/1**, **3/1**, and **4/1**, respectively, should be a reflection of the aromaticity indices for thiophene, pyrrole, and furan, respectively, if the index of benzene is set to 1.00.

The values of the slopes from the plots of the chemical shift values of the carbonyl carbon atoms in **6–8** against those in the benzene compounds **5** also seem to be considered as the indices of aromaticity for the heterocycles. The values 0.86, 0.64, and 0.52 from **6/5**, **7/5**, and **8/5**, respectively, should reflect the magnitude of the direct influence of the heterocyclic rings in comparison with the benzene ring. The values obtained for α -C and β -C from the slopes of the plots **6/5**, **7/5**, and **8/5** may be considered as the indices of the aromaticity for the heterocycles. Although they are slightly different, it is certain that thiophene is most like benzene whereas furan is least like benzene.

In conclusion, it is possible to evaluate the degree of aromaticity of heterocyclic compounds numerically from the slopes of the plot of the ¹³C NMR chemical shift values of the heterocyclic derivatives of chalcones against the chalcone derivatives with same substituents Figure S1–S16.

Acknowledgments. We thank Dr. Gary Kwong for help in preparing the manuscript. This study was supported by 2016 Research Grant from Kangwon National University (No. 520160084).

Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

References

1. See comprehensive reviews: P. Schleyer, *Chem. Rev.* 2001, *101*, 1115 and the articles listed in the issue 5 of *Chem. Rev.* 2001, *101*.

- (a) G. Solomons, C. Fryhle, S. Snyder, Organic Chemistry, 11th ed., Wiley, Hoboken, NJ, 2014, p. 634.
 (b) A. R. Katritzky, M. Karelson, N. Malhotra, Heterocycles 1991, 32, 127. (c) T. M. Krygowski, M. K. Cyranski, Z. Czarnocki, G. Hafelinger, A. R. Ktritzky, Tetrahedron 2000, 56, 1783.
- (a)C. W. Bird, *Tetrahedron* 1985, 41, 1409. (b) C. W. Bird, *Tetrahedron* 1992, 48, 335.
- (a) J. Poater, X. Fradera, M. Duran, M. Sola, Chem. Eur. J. 2003, 9, 400. (b) M. Mandado, M. J. Gonzalez-Moa, R. A. Mosquera, J. Comput. Chem. 2007, 28, 127. (c) A. Fernandez, L. Rincon, R. J. Almeida, Mol. Struct. (Theochem) 2009, 911, 118. (d) A. Mrozek, J. Karolak-Wojciechowska, P. Amiel, J. Barbe, J. Mol. Struct. 2000, 514, 151. (e) M. Mandado, N. Otero, R. A. Mosquera, Tetrahedron 2006, 62, 12204. (f) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. R. Schleyer, Org. Lett. 2006, 8, 863. (g) P. R. Duchowicz, E. A. Castro, J. Theor. Comput. Chem. 2004, 3, 145.
- (a) N. Jadlej-Sosnowska, J. Phys. Org. Chem. 2004, 17, 303.
 (b) M. Giambiagi, M. S. Giambiagi, C. D. S. Silva, A. P. Figueiredo, Phys. Chem. Chem. Phys. 2000, 2, 3381.
- 6. (a) P. R. Duchowicz, E. A. J. T. Castro, Comput. Chem.
 2004, 3, 145. (b) L. Nyulaszi, P. Varnai, T. Veszpremi, J. Mol. Struct. (THEOCHEM) 1995, 358, 55.
 (c) M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, P. R. J. Schleyer, Org. Chem. 2002, 67, 1333.
 (d) F. R. Cordell, J. E. Boggs, J. Mol. Struct. (THEOCHEM) 1981, 85, 163.
- Extensive values are listed inA. R. Katritzky, K. Jug, D. C. Oniciu, *Chem. Rev.* 2001, 101, 1421.
- 8. J. A. Elvidge, Chem. Commun. 1965, 160.
- 9. A. Julg, P. Francois, Theor. Chim. Acta 1967, 8, 249.
- 10. M. J. S. Dewar, Chem. Soc. Spec. Publ. 1967, 21, 177.
- B. S. Hess, L. J. Schaad, J. Am. Chem. Soc. 1973, 95, 3907.
- 12. J. Cioslowski, E. Matito, M. Sola, J. Phys. Chem. A 2007, 11, 6521.
- 13. F. Fringuelli, G. Marino, A. Taticchi, J. Chem. Soc. Perkin Trans. 1974, 2, 332.
- 14. M. Witanowski, Z. Biedrzycka, Magn. Reson. Chem. 1994, 32, 62.
- 15. S. A. N. F. Gomes, R. B. Malion, *Chem. Rev.* 2001, *101*, 1349 and the references therein.
- (a) K. O. Jeon, J. S. Yu, C. K. Lee, *Heterocycles* 2003, 60, 2685.
 (b) C. K. Lee, J. S. Yu, J. S. Park, *Bull. Kor. Chem. Soc.* 2000, 21, 49.
 (c) C. K. Lee, J. S. Yu, H.-J. Lee, *J. Heterocyclic Chem.* 2002, 39, 1207.
 (d) C. K. Lee, J. S. Yu, Y. R. J. Ji, *Heterocyclic Chem.* 2002, 39, 1219.
- 17. C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 1991, 91, 165.
- I.-S. H. Lee, H. J. Jeon, J. S. Yu, C. K. Lee, *Bull. Kor. Chem.* Soc. 2010, 31, 1689.
- I.-S. H. Lee, E. J. Jeoung, C. K. Lee, Bull. Kor. Chem. Soc. 2013, 34, 936.
- A. Perjessy, D. W. Boykin Jr., L. Fisera, A. Krutosikova, J. Kovac, J. Org. Chem. 1973, 38, 1807.
- G. Thirunarayanan, G. Vanangamudi, M. Subramanian, U. Umadevi, S. P. Sakthinathan, R. Sundararajan, *Elixir Org. Chem.* 2011, 39, 4643.
- 22. E. Solaniova, S. Toma, S. Gronowitz, Org. Magnes. Res. 1976, 8, 439.

- S. Bhagat, R. Sharma, D. M. Sawant, L. Sharma, A. K. Chakraborti, J. Mol. Cat. A. 2006, 244, 20.
- 24. D. J. Craik, R. T. C. Brwonlee, Prog. Phys. Org. Chem. 1983, 14, 1.
- 25. R. T. C. Brownlee, D. J. Craik, J. Chem. Soc. Perkin Trans. 1981, 2, 760.
- 26. G. K. Hamer, I. R. Peat, W. F. Reynolds, *Can. J. Chem.* **1973**, *51*, 897.
- 27. C. N. Robinson, G. E. Stablein, C. D. Slater, *Tetrahedron* **1990**, *46*, 335.
- B. Z. Jovanovic, M. Misic-Vukovic, A. D. Marinkovic, J. Csanadi, J. Mol. Struct. 1999, 482-483, 371.

6