J. Serb. Chem. Soc. 69 (10) 749–757 (2004)
JSCS – 3201

UDC 66.092–977+547.915:543.51
Original scientific paper

MS analysis of biindenylidenes

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(Received 17 February 2004)

Abstract: Biindenylidene isomers are components of pyrolysis oils. The mass spectra were recorded and the fragmentation of the following biindenylidene isomers: (*E*)-2,3,2',3'-tetrahydro-[1,1']biindenylidene, (*Z*)-2,3,2',3'-tetrahydro-[1,1']biindenylidene, 1,3,1',3'-tetrahydro-[2,2']biindenylidene and 2,3,1',3'-tetrahydro-[1,2']biindenylidene, as well as of spiro[1,1a,6,6a-tetrahydrocyclopropa[*a*]indene-1,1'-2',3'-dihydro-1'*H*-indene] is discussed.

Keywords: mass spectrometry, fragmentation, biindenylidenes.

INTRODUCTION

Biindenylidenes are, as derivatives of indene, among the important components of the pyrolysis oils and their MS data could be useful in environmental research.[1,2] They are also very appropriate model substances for NMR and X-ray analysis. Theoretically, there are four biindenylidene isomers (Fig. 1): (*E*)-2,3,2',3'-tetrahydro-[1,1']biindenylidene (structure **1**),[3,4] (*Z*)-2,3,2',3'-tetrahydro-[1,1']biindenylidene (structure **2**),[3,5] 1,3,1',3'-tetrahydro-[2,2']biindenylidene (structure **3**)[3,6] and 2,3,1',3'-tetrahydro-[1,2']biindenylidene (structure **4**)[3,7]. The MS data of spiro[1,1a,6,6a-tetrahydrocyclopropa[*a*]indene-1,1'-2',3'-dihydro-1'*H*-indene][8] (structure **5** in Fig. 1) are also presented in this work. It is an indene dimer without a double bond and is of interest for comparison. All five isomers have been described in the literature but their mass spectrometry have not been discussed hitherto.

EXPERIMENTAL

(E)-*2,3,2',3'-Tetrahydro-*[*1,1'*]*biindenylidene* (**1**) Compound **1** was synthesized through the reductive coupling of 1*H*-indan-1-one according to the method of Lenoir and Lemmen[9] and isolated as yellow crystals (m.p. 418 K) by crystallization from propan-2-ol. The structure was confirmed by X-ray analysis.[4]

(Z)-*2,3,2',3'-Tetrahydro-*[*1,1'*]*biindenylidene* (**2**). Compound **2** was isolated from the above product mixture[9] by two-step chromatography using column chromatography in the first and HPLC in the second step. Recrystallization from propan-2-ol gave colourless crystals (m.p. 328 K). The structure was confirmed by X-ray analysis.[5]

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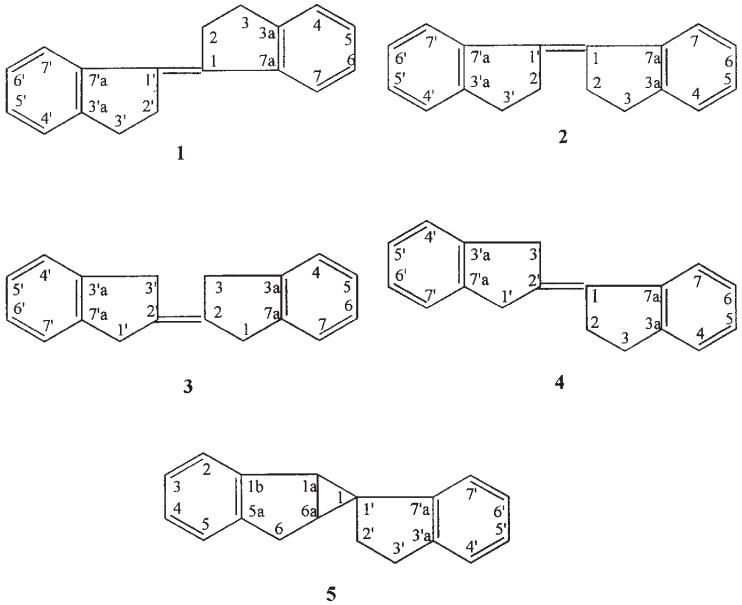

Fig. 1. Compounds studied.

1,3,1',3'-Tetrahydro-[*2,2'*]*biindenylidene* (**3**). Compound **3** was synthesized by reductive coupling of 1-*H*-indan-2-one and crystallized (colourless crystals m.p. 448 K) following the method described by Czogalla and Boberg.[10] The structure was confirmed by X-ray analysis.[6]

2,3,1',3'-Tetrahydro-[*1,2'*]*biindenylidene* (**4**). Compound **4** was isolated from the product mixture obtained by reaction of 1*H*-indene with H_2SO_4[2] by HPLC on a preparative normal phase column (VP 250/10 Nucleosil 100-7) by isocratic LC elution using *n*-hexane. Recrystallization from propan-2-ol gave colorless crystals (m.p. 359 K). The structure was confirmed by X-ray analysis.[7]

Spiro[*1,1a,6,6a-tetrahydrocyclopropa*[a]*indene-1,1'-2',3'-dihydro-1'*H-*indene*] (**5**). Compound **5** was synthesized in two steps according to the method of Bell and Spanswick.[11] In the first step, the aldol condensation of 1*H*-indan-1-one was accomplished and the self-condensation carbonyl product was reduced in the second step by the Huang-Minlon reduction. The final product was isolated by crystallization (m.p. 367 K) from propan-2-ol. The structure was confirmed by X-ray analysis.[8]

MS-spectra

A GC-MS Shimadzu GC 17A and a Shimadzu QP 5000 were used.

Gas chromatography: on-column injection (temperature 60–295 ºC); column DB-5, 30 m, 0.25 μm i.d.; μm i.d. FT; flow 0.8 ml He/min; temperature program 60 ºC (5 min) – 4 ºC/ min – 300 ºC (30 min); interface 280 ºC.

Mass spectrometry: EI ionisation energy: 70 eV; vacuum: 1.5×10^{-3} Pa; ion source 200 ºC; detector gain was set to 1.75 kV; mass range 45 – 700 u.

RESULTS AND DISCUSSION

Compounds **1 – 5** show similar mass spectra. In the region under *m*/*z* 100 they are nearly identical showing only slight differences of relative abundances (RA) of the ions. Above *m*/*z* 100, five abundant peak groups are presented with the RA of the highest peak of the group being above 10 %, at least in one of the compounds **1 – 5**. The most prominent ions of the groups are: *m*/*z* 232 (M^+); *m*/*z* 217/215; *m*/*z* 202; *m*/*z* 117/116/115 and *m*/*z*

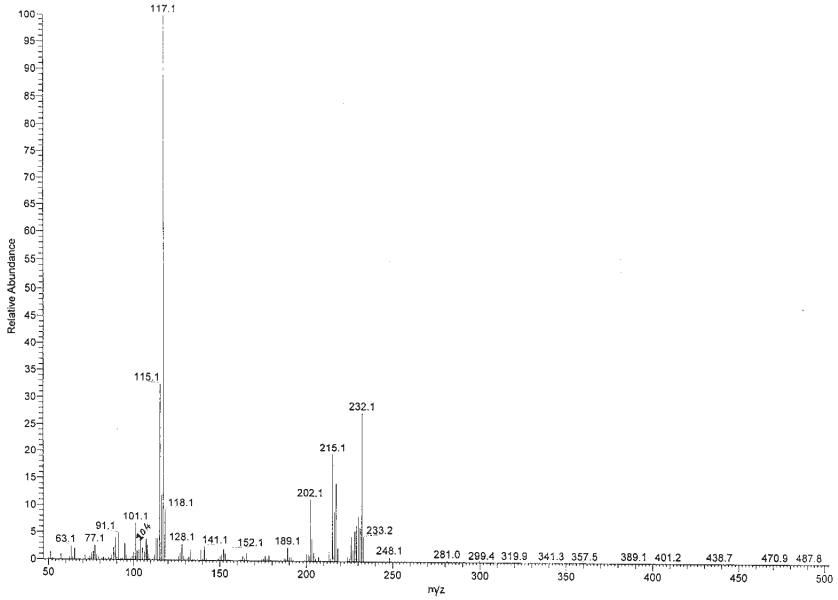

Fig. 2. Mass spectrum of compound **4**.

104/101. They can be seen in Fig. 2 which represents the mass spectrum of compound **4** which is shown as an example. The RA of the ions of the five groups are presented in Table I. Table II shows the RA of the ions of group *m/z* 232 (M^+).

TABLE I. Relative abundances (%) of the five groups of highest peaks

Compound	*m/z*								
	232	217	215	202	117	116	115	104	101
1	100	78	37	21	84	4	45	2	8
2	100	82	29	28	91	4	48	2	12
3	56	13	15	10	20	100	28	20	7
4	28	15	20	11	100	12	32	3	6
5	30	13	15	14	100	2	29	3	5

TABLE II. Relative abundances (%) of peaks around M^+ (*m/z* = 232)

Compound	*m/z*								
	232	231	230	229	228	227	226	225	224
1	100	5	5	6	4	3	5	1	1
2	100	1	5	7	3	3	6	1	1
3	56	6	6	6	2	3	4	1	1
4	28	6	8	6	5	2	4	1	1
5	30	0	2	4	3	1	4	1	1

Group m/z *232 (M^+)*

The highest peak of this group is the molecular ion (see Fig. 2 and Tables). It is the base peak of compounds **1** and **2**. The explanation for this could be that the positive charge of their molecular ions is stabilized by conjugation of the double bond with both benzene rings. Compounds **1** and **2** gave nearly identical mass spectra with some small differences of the RA of ions *m/z* 215 and 202 (see Table I) and ion *m/z* 231 (see Table II). This confirms that the double bond had been ionized, enabling free rotation and giving practically the same molecular ion.

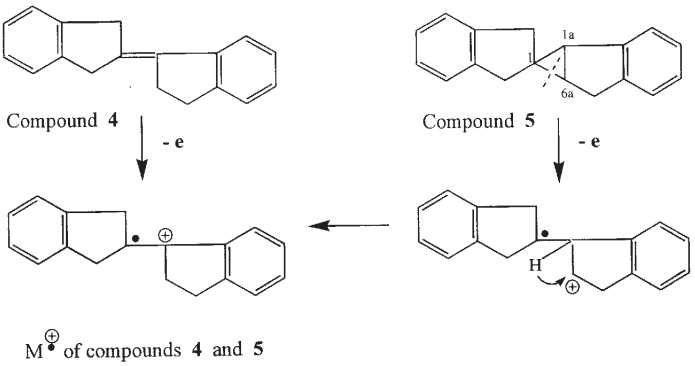

Fig. 3. Molecular ion structures of compounds **4** and **5**.

The RA of the molecular ions of compounds **4** and **5** is practically the same (RA 28 and 30 %, respectively). They also have nearly identical mass spectra with some small differences in the ratio of the RA of ions *m/z* 232, 215 and 202 and higher differences of the RA of ions *m/z* 231 (see Table II) and *m/z* 116. They could have the same molecular ion, as is shown in Fig. 3. The high symmetrical compound **3** gave a more stable molecular ion (RA 56 %) compared to compounds **4** and **5** (RA 28 and 30 %, respectively). The explanation for this could be that in compound **3** there is no possibility for cleavage of any C – C bond, which would require a simultaneous benzylic and allylic cleavage. This cleavage is the first and the most abundant fragmentation in compounds **1**, **2**, **4** and **5** (see Figs. 4 – 6).

The group *m/z* 232 (M^+) shows eight small peaks beginning with $(M-1)^+$ and ending with $(M-8)^+$ (see Fig. 2 and Table II). Obviously, all the eight aliphatic H are involved in the consecutive losses of $H^\bullet$ and H_2. Compound **5** is an exception showing no $(M-1)^+$ ion. The explanation for this could be that it is the only one not having an allylic H and, consequently, H_2 is lost in the first fragmentation step. One of the rare differences in the spectra of compounds **1** and **2** is the RA of ion *m/z* 231 being much higher in the spectrum of compound **1** (RA 5 and 1 %, respectively).

Group m/z *217/215*

The ion *m/z* 217 is highly abundant in the mass spectra of compounds **1** and **2** (RA 78 and 82 %, respectively). Its RA in compounds **3 – 5** amounted to only 13, 15 and 13 %, respectively. The explanation for this could be that compounds **1** and **2** have two $–CH_2–CH_2–$ structural elements. The cleavage of this C – C bond is the first fragmentation step toward the elimination of a CH_3 radical. The fragmentation mechanism of building ions *m/z* 217 is shown in Figs. 4 – 6.

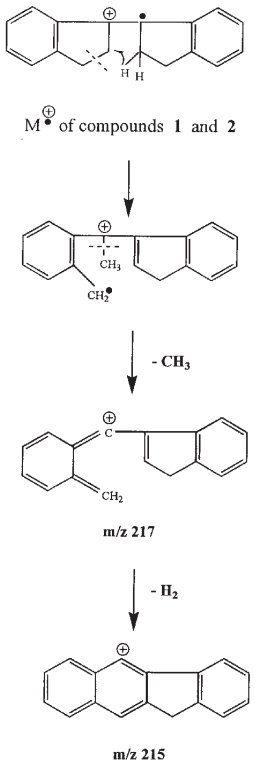

Fig. 4. Fragmentation mechanism of the formation of ions *m/z* 217 and 215 from compounds **1** and **2**.

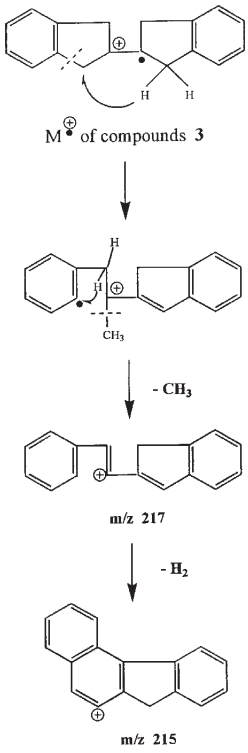

Fig. 5. Fragmentation mechanism of the formation of ions 217 and 215 from compound **3**.

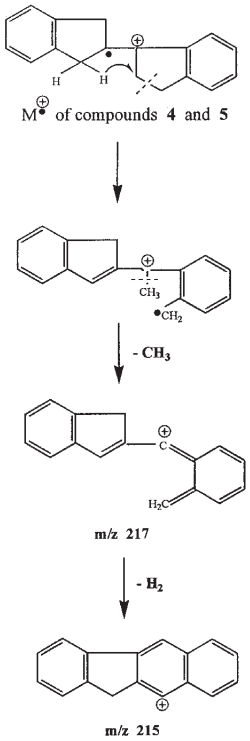

FIg. 6. Fragmentation mechanism of the formation of ions *m/z* 217 and 215 from compounds **4** and **5**.

The ions *m/z* 215 are built from ions *m/z* 217 through a cyclization reaction and a H_2 loss (see Figs. 4 – 6).

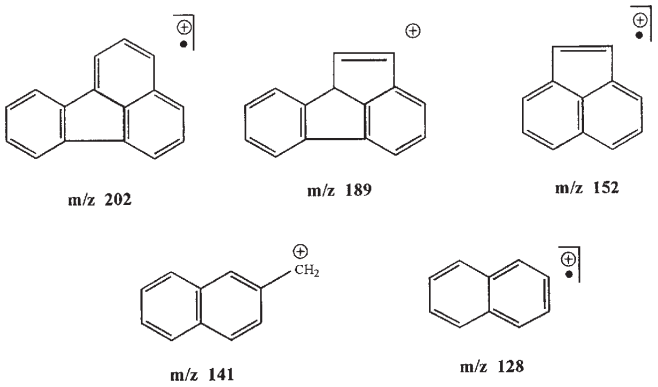

Fig. 7. Condensed structure ions.

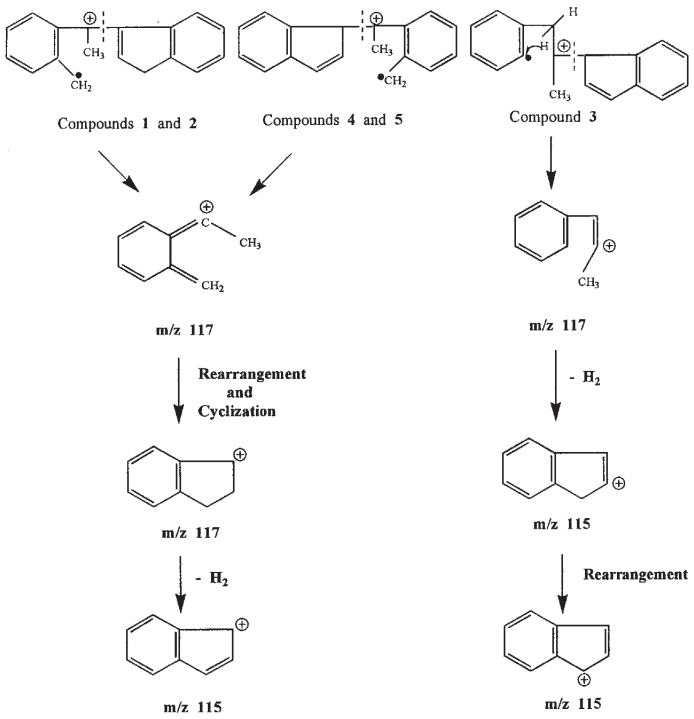

Fig. 8. Fragmentation mechanism of the formation of ions *m/z* 117 and 115 from compounds **1** – **5**.

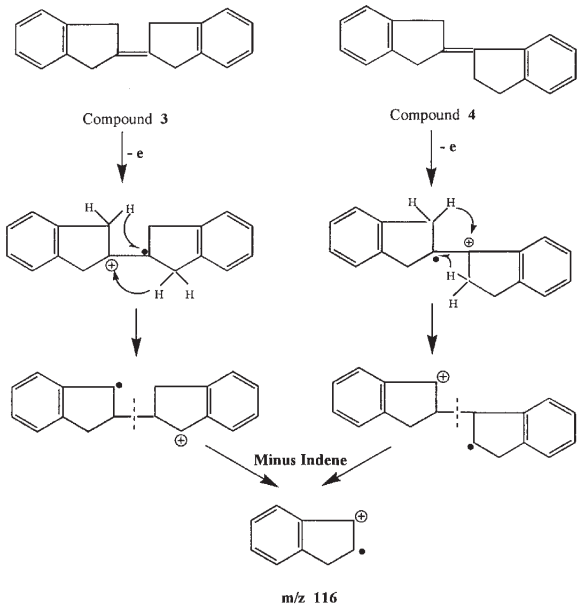

Fig. 9. Fragmentation mechanism of the formation of ion *m/z* 116 from compounds **3** and **4**.

Group m/z *202*

This ion could arise *via* loss of $CH_2 = CH_2$ and H_2 from the molecular ion by a combination of fragmentation, rearrangement and cyclization. The result is usually a more condensed structure ion as is shown in Fig. 7. In the mass spectra of compounds **1** – **5**, there are small peaks (RA less than 3 %) at *m/z* 189, 152, 141 and 128 which also represent condensed structure ions (see Fig. 7).

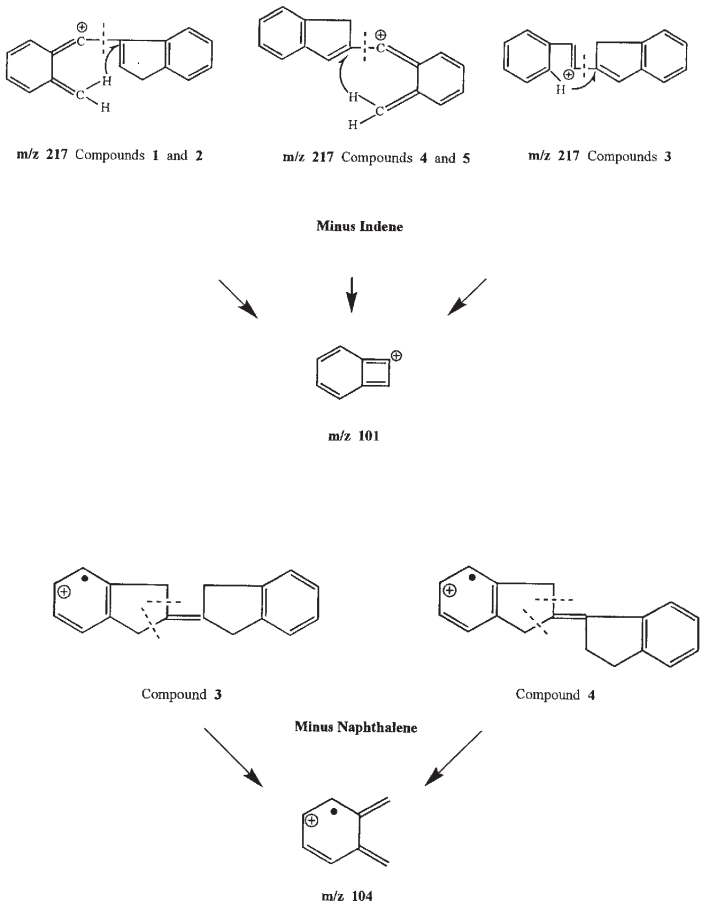

Fig. 10. Fragmentation mechanism of the formation of ions *m/z* 101 and 104 compounds **3** and **4**.

Group m/z *117/116/115*

Ions *m/z* 117 could be formed directly from the molecular ions of compounds **1** – **5** by elimination of an indene radical, instead of a CH_3 radical. Ions *m/z* 115 could be obtained from ions *m/z* 117 by a loss of H_2 (See Fig. 8). In the mass spectra of compounds **4** and **5**, the ion *m/z* 117 is the base peak and it is the second most abundant ion in the mass spectra of compounds **1** and **2** (RA 84 and 91 %, respectively). These results, as well as the RA values of ion *m/z* 215, which do not differ much in compounds **1**, **2**, **4** and **5**, indicate the

same fragmentation route (see Fig. 8). In the mass spectrum of compound **3**, the RA of ion *m*/*z* 115 (RA 28 %) is higher than RA of *m*/*z* 117 (RA 20 %). This indicates the formation of a less stable ion *m*/*z* 117 (see Fig. 8).

Ion *m*/*z* 116 is present only in the mass spectra of compounds **3** (base peak) and **4** (RA 12 %), the double bonds of which are formed from carbon atoms C2–C2' and C2'–C1, respectively (see Fig. 1). The fragmentation mechanism of the formation of ion *m*/*z* 116 is shown in Fig. 9.

Group m/z *104/101*

The fragmentation mechanism of the formation of ion *m*/*z* 101 is shown in the upper part of Fig. 10. This fragmentation is energetically favoured by the elimination of the indene molecule. Ion *m*/*z* 104 is significantly abundant only in the mass spectrum of compound **3** (RA 20 %). The fragmentation mechanism of the formation of this ion is shown in the lower part of Fig. 10. Ion *m*/*z* 116 could be, theoretically, formed also from compound **4** (see Fig. 10) but is present in its mass spectrum only with a RA of 3 %. Obviously, the ionization of the double bond of compound **4**, which gives a benzylic-type ion, is preferred to the ionization of the double bond in the benzene ring. Ionization of the double bond of compound **3**, on the contrary, can not give a benzylic-type ion and could therefore make the ionization in the benzene ring concurrent.

CONCLUSION

The mass spectra of biindenylidene isomers, as well as of spiro[1,1a,6,6a-tetrahydrocyclopropa[*a*]indene-1,1'-2',3'-dihydro-1'*H*-indene] differ sufficiently from each other to make their identification in complex mixtures possible by comparison with the authentic mass spectra presented in this work. The similarity of their mass spectra was, however, so great that they could not be used to prove the individual structures unambiguously. For this purpose ^{1}H, ^{13}C and 2D NMR and X-ray analysis must be used.

Acknowledgements: We thank the German Academic Exchange Service (DAAD) Bonn, Germany, for supporting the work in this paper through a fellowship to S. Sinadinović-Fišer and J. Jovanović.

ИЗВОД

MS АНАЛИЗА БИИНДЕНИЛИДЕНА

СНЕЖАНА СИНАДИНОВИЋ-ФИШЕР[1] и ЈОВАН ЈОВАНОВИЋ[2]

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Масени спектри четири изомерна биинденилидена: (*E*)-2,3,2´,3´-тетрахидро-[1,1']биинденилидена, (*Z*)-2,3,2´,3´-тетрахидро-[1,1']биинденилидена, 1,3,1´,3´-тетрахидро-[2,2']биинденилидена и 2,3,1´,3´-тетрахидро-[1,2']биинденилидена, као и једињења спиро[1,1a,6,6a-тетрахидроциклопропа[*a*]инден-1,1´-2´,3´-дихидро-1´*H*-индена] су снимљени и дискутовани. Као деривати индена, биинденилидени се налазе међу компонентама пиролитичких уља и њихови масени спектри су корисни у анализи загађивача животне средине. Они, истовремено, представљају згодне модел-супстанце за NMR и анализу помоћу X-зрака. Поред четири теоријски могућа

изомера биинденилидена, у раду се дају и MS подаци за једињење: спиро[1,1a,6,6a-тетрахидроциклопропа[*a*]инден-1,1´-2´,3´-дихидро-1´*H*-инден]. То је димер индена који нема двоструку везу и интересантан је за поређење. Свих пет изомера је описано у литератури, али дискусија њихових масених спектара није до сада приказана. Масени спектри изомера биинденилидена, као и једињења спиро[1,1a,6,6a-тетрахидроциклопропа[*a*]инден-1,1´-2´,3´-дихидро-1´*H*-индена], довољно се међусобно разликују да се сваки од њих може поуздано идентификовати у сложеним смешама поређењем са аутентичним спектрима приказаним у овом раду. Међусобне сличности њихових масених спектара су, међутим, толико велике да их није било могуће користити за одређивање коначних структура ових изомера. За то се морају користити ^{1}H, ^{13}C и 2D NMR анализа, као и анализа помоћу X-зрака.

(Примљено 17. фебруара 2004)

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