

## NMR Analysis of 2-(2', 3'-dihydro-1'H-inden-1'-yl)-1H-indene\*

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<sup>1</sup>H, <sup>13</sup>C and two dimensional NMR analyses were applied to determine the NMR parameters of 2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene. The chemical shifts of all the H- and C-atoms, as well as the appropriate coupling constants were determined and the complete NMR resonance assignments of the molecule are given. The predicted patterns of the four different H atoms of the two methylene groups of the indane structural element coincided completely with the complex patterns in the NMR spectra.

*Keywords:* NMR spectroscopy, structure elucidation; dimers of indene.

### INTRODUCTION

The reaction of indene in the presence of Friedel-Crafts acids gives a product mixture containing dimers, trimers and higher oligomers.<sup>1,2</sup> Their yield and relative quantity depends highly on the reaction temperature and the acid used. The main component of the dimer fraction is 2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene. This compound has been described in the literature<sup>3,4</sup> but has not been analysed by NMR in detail. It was shown in this study that this compound represents an interesting model substance for NMR analysis. It was possible to determine the most important NMR parameters and to give unambiguous proof of its chemical structure. Derivatives of indene are among the major components of the pyrolysis oils and their NMR data could be useful in environmental research.

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\* Dedicated to Professor Dragutin M. Dražić on the occasion of his 70th birthday.

# Serbian Chemical Society active member.

## EXPERIMENTAL

*2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene*

The compound was isolated by HPLC from the reaction mixture obtained by reacting indene in the presence of H<sub>2</sub>SO<sub>4</sub>, as has been described earlier.<sup>2</sup>

*NMR analysis*

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were acquired in CDCl<sub>3</sub> on a Bruker AMX 600 spectrometer: The <sup>1</sup>H-(frequency: 600.13 MHz) NMR spectra were internally referenced to the residual CHCl<sub>3</sub> signal (7.26 ppm) and the <sup>13</sup>C-(frequency: 150.94 MHz) NMR spectra to the CDCl<sub>3</sub> signal (77.70 ppm). A 5 mm multinuclear probe with a z-gradient was used for the standard 1D <sup>1</sup>H experiments and 2D (COSY, HMQC, HMBC) experiments. A <sup>13</sup>C sensitive dual probe was used for the 1D <sup>13</sup>C-NMR experiments. The 1D <sup>13</sup>C spectra were acquired with a sweep width of 35000 Hz in 64 K data points with zero filling to 128 K. The relaxation delay was 1.5 s.

## RESULTS AND DISCUSSION

The structure of 2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene with the usual assignment of the C-atoms is shown in Fig. 1 and its <sup>1</sup>H-NMR spectrum in Fig. 2.

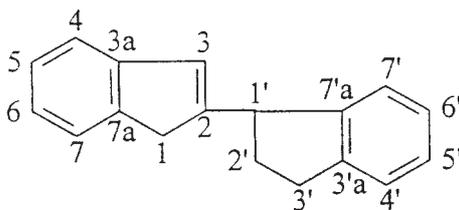


Fig. 1. Structure of 2-(2', 3'-dihydro-1'H-inden-1'-yl)-1H-indene with the assignment of the C-atoms used in this study.

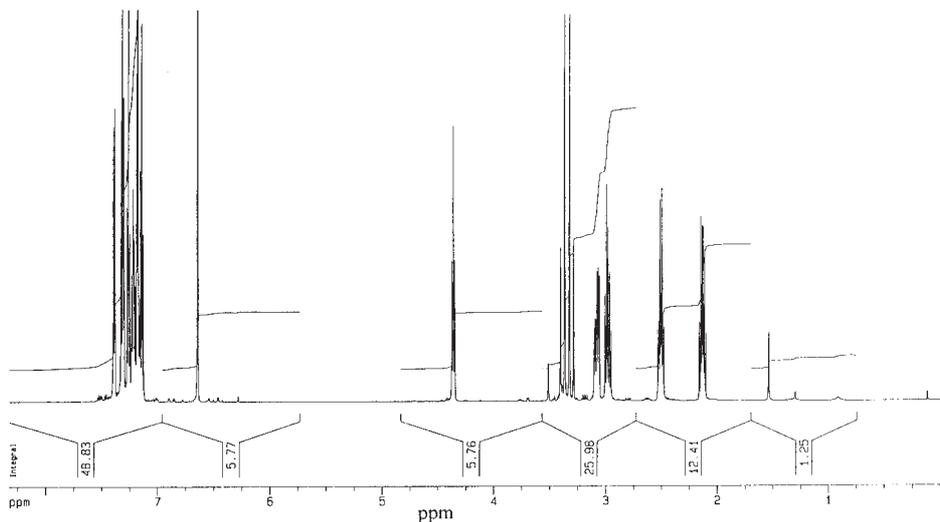


Fig. 2. <sup>1</sup>H-NMR spectrum of 2-(2', 3'-dihydro-1'H-inden-1'-yl)-1H-indene.

The following peaks originated from the investigated sample: four multiplets from 4H at 2.13; 2.50; 2.98 and 3.08 ppm; AB system doublet from 2H at 3.31 and 3.38 ppm; a triplet from 1H at 4.36 ppm; a singlet from 1H at 6.64 ppm and aromatic H atoms at 7.14 – 7.39 ppm.

On the basis of a comparison with the  $^1\text{H}$ -NMR spectra of indene, indane and diphenylmethane,<sup>5</sup> it was possible to locate the following H atoms.

2H on C-1 – 3.31 and 3.38 ppm, (in the case of indene distorted singlet at 3.35 ppm). The H-atoms of the  $\text{CH}_2$  group of the indene structural element are not equivalent, as in indene. This is a consequence of the influence of the substitute on C-2. They represent an AB system and create two typical doublets centered at 3.31 and 3.38 ppm (see Fig. 2). The Differential Functional Theory (DFT) calculation of the structure shown in Fig. 1 gave clearly different values of the natural charge of these two H-atoms;<sup>6</sup> 1H on C-3 – 6.64 ppm, singlet; 1H on C-1' – 4.36 ppm, triplet (in the case of diphenylmethane singlet at 3.95 ppm); 2H on C-2' – 2.13 and 2.50 ppm, multiplets (in the case of indane peak at 2.09 ppm); 2H on C-3' – 2.98 and 3.08 ppm, multiplets (in the case of indane peak at 2.90 ppm).

Due to the free rotation of the  $\text{sp}^2 - \text{sp}^3 \text{C}-\text{CH}$  bond between C-2 and C-1' all the four H-atoms of the methylene groups of the indane structural element are chemically non-equivalent and, due to the chiral C-1' atom, diastereotopic. This was confirmed by the DFT calculation, giving clearly different values of the natural charge for these H-atoms.<sup>6</sup> Therefore, they have different chemical shifts and show geminal and vicinal coupling being present as four complex multiplets, as can be seen in Fig. 3.

The H-atoms of C-3' differ in chemical shift by only 0.1 ppm, *i.e.*  $\Delta\nu = 60$  Hz in this particular case. Their geminal coupling constant was  $^2J_{\text{HH}} = 15.7$  Hz (see Fig. 4) and  $\Delta\nu/J = 60/15.7 = 3.8$ . Consequently, they must give an AB pattern. Both of them must show vicinal coupling with the H-atoms on C-2'. Fig. 4a shows that in the case of the H-atom with a chemical shift of 3.08 ppm, the vicinal coupling constants  $^3J_{\text{HH}}$  were

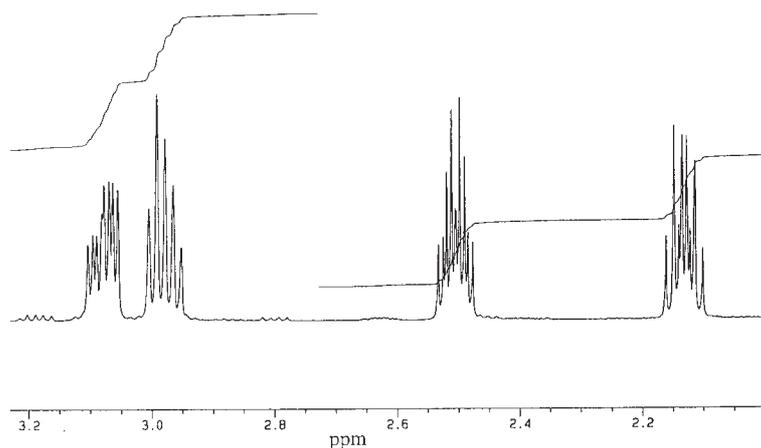


Fig. 3. The four multiplets of the H atoms of the methylene groups of the indane structural element.

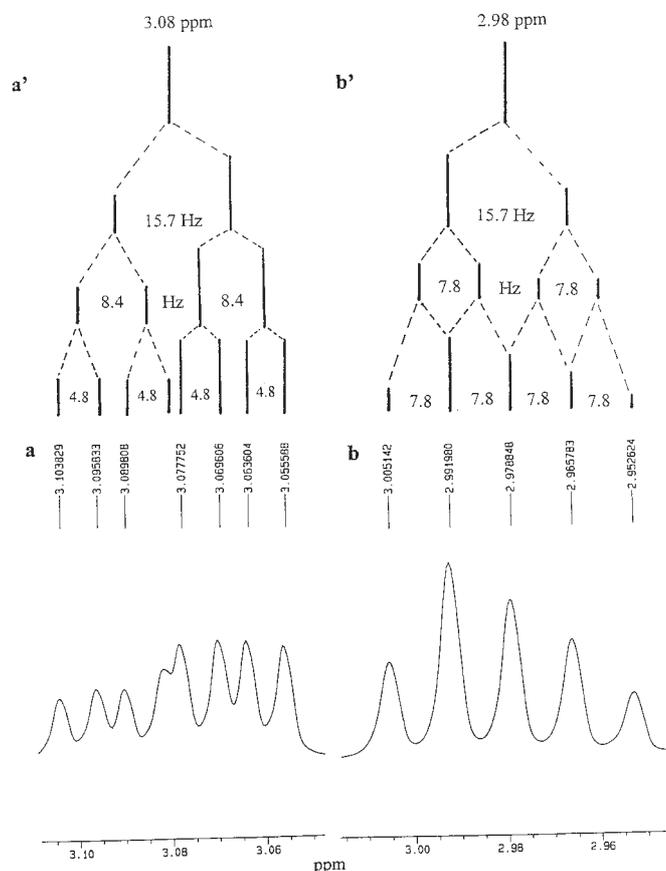


Fig. 4. Patterns of the H-atoms with chemical shifts 3.08 ppm (Fig. 4a) and 2.98 ppm (Fig. 4b) that were located on C-3' and the predicted patterns (Figs. 4a' and 4b').

8.4 and 4.8 Hz, respectively. The predicted pattern is then like that illustrated in Fig. 4a', which coincides with the pattern of the  $^1\text{H}$ -NMR spectrum shown in Fig. 4a.

In the case of the H-atom with a chemical shift of 2.98 ppm, the vicinal coupling constants (see Fig. 4b)  $^3J_{\text{HH}}$  were the same, *i.e.*, 7.8 Hz. The predicted pattern (see Fig. 4b') coincides with the pattern of the NMR spectrum shown in Fig. 4b.

The pattern of the H-atoms on C-2' must be more complex, as in addition to the geminal coupling and the vicinal coupling with the H-atoms on C-3', there is also a vicinal coupling with the H-atom on C-1'. The chemical shift difference of these H-atoms ( $2.50 - 2.13 = 0.37$  ppm) is, however, much larger than in the previous case and it amounts to 222 Hz in this particular case. Consequently, the  $\Delta\nu/J$  is greater than 10 and the obtained patterns are not distorted, *i.e.*, they are symmetrical in relation to the vertical axes passing through the middle point of the patterns (see Fig. 5a and 6a).

Figures 5 and 6 show that the geminal coupling constant  $^2J_{\text{HH}}$  of the H-atoms on C-2' is 12.6 Hz. They must give an AX pattern. Both of them must show vicinal cou-

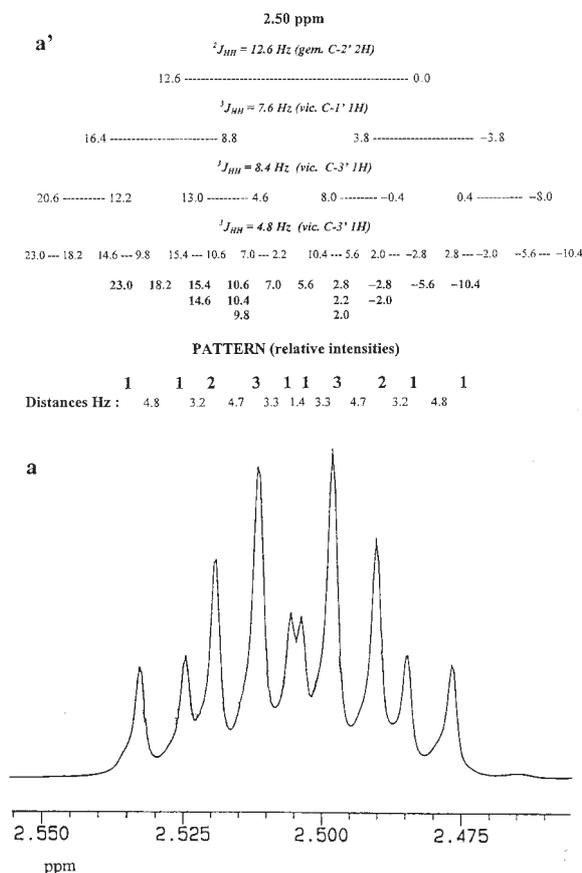


Fig. 5. Pattern of the H-atom with chemical shift 2.50 ppm (Fig. 5a) that was located at C-2' and the predicted pattern (Fig. 5a').

pling with the H-atoms on C-3' with the already given values of  $^3J_{HH}$  (8.4 and 4.8, and two times 7.8 Hz, respectively). The triplet of H-atoms on C-1' showed the same vicinal coupling constant with both of the H-atoms on C-2' having the value:  $^3J_{HH} = 7.6 \text{ Hz}$ .

Taking all these facts into account, the predicted patterns of the H-atoms on C-2' are shown in Figs. 5a' and 6a'. As can be seen they coincide with the patterns of the  $^1\text{H-NMR}$  spectra shown in Figs. 5a and 6a completely, in terms of both the intensities of the peaks and the distances between them.

The COSY spectrum in the region 2.0 – 4.5 ppm showed clearly the coupling between following H-atoms: H (4.36 and 2.50 ppm); H (4.36 and 2.13 ppm); H (3.38 and 3.31 ppm); H (3.08 and 2.98 ppm); H (3.08 and 2.50 ppm); H (3.08 and 2.13 ppm); H (2.98 and 2.50 ppm); H (2.98 and 2.13 ppm); H (2.50 and 2.13 ppm).

The COSY spectrum in the region 3.2 – 7.5 ppm showed clearly that there is no coupling with the H-atom on C-3 (6.64 ppm). The chemical shifts and patterns of the seven aromatic H-atoms, as is shown in Fig. 7, are as follows: at 7.39 ppm – 1H doublet; at 7.32 ppm

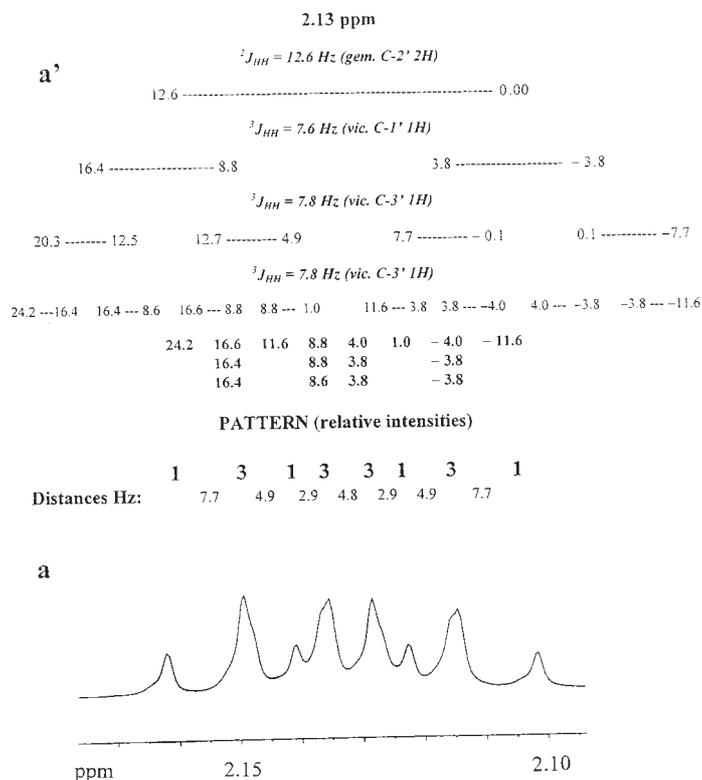


Fig. 6. Pattern of the H-atom with chemical shift 2.13 ppm (Fig. 6a) that was located at C-2' and the predicted pattern (Fig. 6a').

– 1H doublet; the high field peak of the doublet coincides with the low field peak of the doublet at 7.31 ppm; at 7.31 ppm – 1H doublet; the low magnetic field peak of the doublet coincides with the high field peak of the doublet at 7.32 ppm; at 7.26 ppm – 1H triplet; the peak in the middle coincides with the peak of  $\text{CHCl}_3$ ; at 7.22 ppm – 1H triplet; distorted; at 7.20–7.17 ppm – 2H peaks; the pattern is complex and the chemical shift difference between H-atoms is below 0.01 ppm. If they are coupling with each other they would represent an AB system with two high inner peaks. The lower field inner peak could belong to the H-atom which undergo vicinal coupling with another H-atom giving practically a doublet with the higher field peak overlapped with the higher field inner peak. In that case the chemical shifts of these two H-atoms are 7.18 and 7.17 ppm, respectively, and at 7.14 ppm – 1H triplet distorted.

The  $^{13}\text{C}$  spectrum in the region 25 – 155 ppm obtained by DEPT experiment is shown in Fig. 8. Three peaks originating from the three  $\text{sp}^3 \text{CH}_2$  groups (32.2; 34.2 and 39.1 ppm) and one peak originating from the  $\text{sp}^3 \text{CH}$  group (47.8 ppm) are present. The  $^{13}\text{C}$  peaks of the aromatic and the olefinic  $\text{sp}^2 \text{CH}$  are in the regions 120 – 130 ppm with the following chemical shifts: 120.6; 124.0; 124.3; 124.9; 125.1; 126.7; 126.7; 127.1 and 127.7 ppm. The group of the five less intensive peaks in the region 140 – 155 ppm

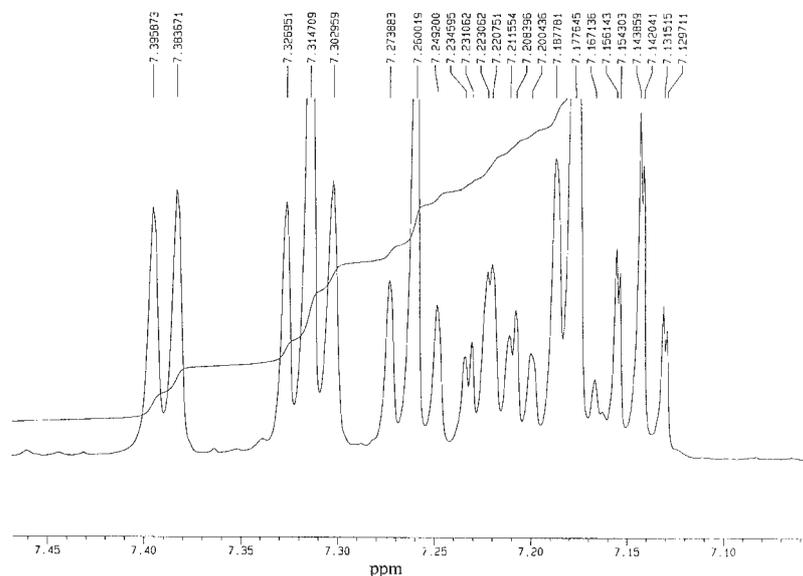


Fig. 7.  $^1\text{H}$ -NMR spectrum in the region 7.10 – 7.45 ppm.

represents the quaternary C- atoms at 143.7; 144.3; 145.6; 146.2 and 152.9 ppm. The exceptionally large chemical shift of the quaternary C-atom at 152.9 ppm indicates an alkyl-substituted olefinic C-atom,<sup>5</sup> as is the C-2.

The couplings between the following C- and H-atoms were determined on the basis of the  $^1\text{H}$  –  $^{13}\text{C}$  COSY spectrum (HSQC experiment): C-atom at 32.2 and 1H-atom at 3.08 and 1H-atom at 2.98 ppm; C-atom at 34.2 and 1H-atom at 2.50 and 1H-atom at 2.13 ppm; C-atom at 39.1 and 1H-atom at 3.31 and 1H-atom at 3.38 ppm; C-atom at 47.8 and 1H-atom at 4.36 ppm; C-atom at 120.6 and 1H-atom at 7.32 ppm; C-atom at 124.0 and 1H-atom at 7.39 ppm; C-atom at 124.3 and 1H-atom at 7.14 ppm; C-atom at 124.9 and 1H-atom at 7.31 ppm; C-atom at 125.1 and 1H-atom at 7.17 ppm; C-atom at 126.7 and 1H-atom at 7.26 ppm; C-atom at 126.7 and 1H-atom at 7.22 ppm; C-atom at 127.1 and 1H-atom at 7.18 ppm; and C-atom at 127.7 and 1H-atom at 6.64 ppm.

These data enabled all the C-atoms of the  $\text{sp}^3\text{CH}_2$  groups and the  $\text{sp}^3\text{CH}$  group, as well as of the olefinic C-atoms (C-2 at 152.9 and C-3 at 127.7 ppm) to be located, as given in the Table I and Fig. 9. To locate the aromatic H- and C- atoms, the COSY spectrum of the aromatic H-atoms and the long range  $^1\text{H}$  –  $^{13}\text{C}$  COSY (HMBC experiment) spectra were required. The COSY spectrum of the aromatic H-atoms showed coupling between the following H-atoms: H 7.39 and H 7.14 ppm; H 7.32 and H 7.26 ppm; H 7.26 and H 7.14 ppm; H 7.31 and H 7.22 ppm; H 7.22 and H 7.18 ppm; H 7.18 and H 7.17 ppm.

The HMBC experiment showed long range  $^1\text{H}$  –  $^{13}\text{C}$  COSY coupling between the quaternary C-atoms at 143.7 and 145.6 ppm and both of the H-atoms at 3.31 and 3.38 ppm. It proved that these C-atoms belong to the indene structural element (C-3a and C-7a). The exceptionally low chemical shift of the aromatic CH C-atom at 120.6 ppm indicates the position C-4, as in the case of indene (C-4 at 120.9 ppm).<sup>5</sup> Consequently, the

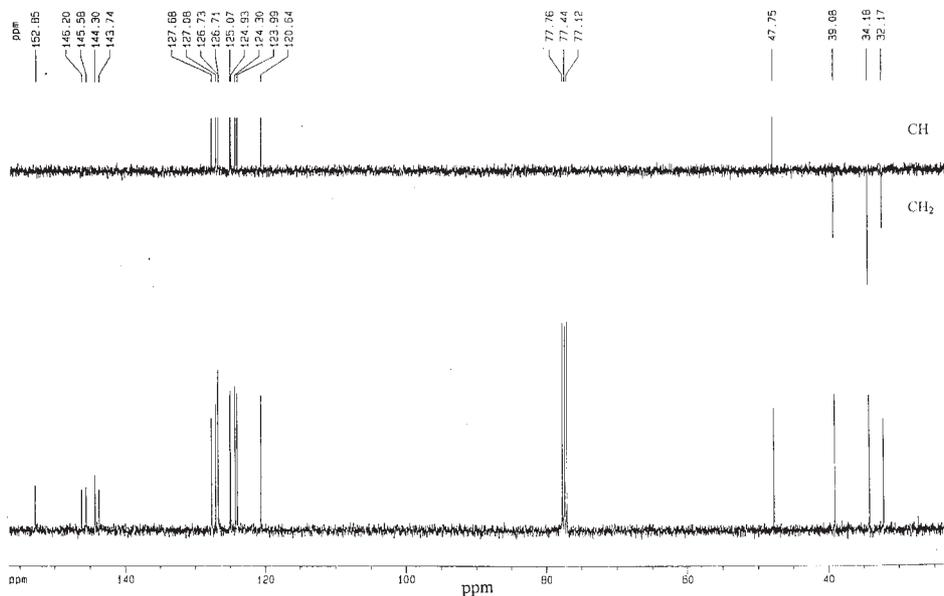


Fig. 8.  $^{13}\text{C}$ -NMR spectrum in the region 25 – 155 ppm. The upper spectrum was obtained by DEPT experiment.

chemical shift of the H-atoms on C-4 is 7.32 ppm (see the result of the HSQC experiment). The H-atom (doublet) at 7.32 ppm couples with the H-atom (triplet) at 7.26 ppm and, hence, is located on C-5 having a chemical shift of 126.7 ppm. Using the same logic, the assignments on C-6 and C-7 were made as shown in the Table I and Fig. 9.

The HMBC experiment showed long range  $^1\text{H} - ^{13}\text{C}$  COSY coupling between the quaternary C-atoms at 145.6 ppm and the H-atom (7.26 ppm) on C-5. Consequently, the quaternary C-atoms C-3a and C-7a have chemical shifts of 145.6 and 143.7 ppm, respectively. This was confirmed by the long range coupling of  $^1\text{H}$  at 7.14 and  $^{13}\text{C}$  at 143.7 ppm. The HMBC experiment showed long range  $^1\text{H} - ^{13}\text{C}$  COSY coupling between the quaternary C-atoms at 144.3 and 146.2 ppm and H-atom at 4.36 ppm (triplet). It proved that they belong to the indane structural element (C-3'a and C-7'a). As the chemical shift of the quaternary C-atoms becomes greater if they are bonded with  $\text{sp}^3$   $\text{CH}_3$ ,  $\text{CH}_2$ , CH and quaternary C-atom, respectively,<sup>5</sup> the peaks at 146.2 and 144.3 ppm were assigned to C-7a' (bonded to CH) and C-3'a (bonded to  $\text{CH}_2$ ), respectively.

The HMBC experiment showed the correlation peak for the C-3' (32.2 ppm) and H-atom at 7.31 ppm. Therefore, this H-atom must be on C-4'. On the basis of this information, the COSY spectrum of aromatic H-atoms and the HMBC experiment which showed the long range coupling of  $^1\text{H}$  at 7.22 and  $^{13}\text{C}$  at 144.3 ppm, but not with  $^1\text{H}$  at 7.18 ppm, and of  $^1\text{H}$  at 7.18 and  $^{13}\text{C}$  at 146.2 ppm, but not with  $^1\text{H}$  at 7.22, it was possible to assign the aromatic C- and H-atoms of the indane structural element as shown in

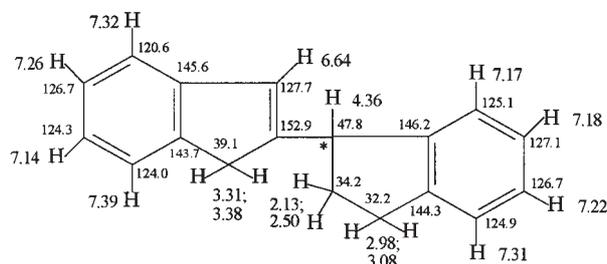


Fig. 9. Chemical shifts (ppm) of the H- and C-atoms of 2-(2', 3'-dihydro-1'H-inden-1'-yl)-1H-indene.

the Table I and Fig. 9. The coupling constants were determined as usual on the basis of the <sup>1</sup>H-NMR spectra.

As depicted in the Table I and Fig. 9, it was possible, on the basis of the described analysis, to locate the chemical shifts of all the C and H atoms of 2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene, and to give the values of the appropriate coupling constants  $J_{HH}$  (see the Table I).

TABLE I. Chemical shifts  $\delta$ [ppm] of the H- and C-atoms and  $J_{HH}$  coupling constants of 2-(2', 3'-dihydro-1'H-inden-1'-yl)-1H-indene

C-atom	<sup>13</sup> C	<sup>1</sup> H	$J_{HH}$	HMBC experiment		Remark
	$\delta$	$\delta$		Hz	<sup>2</sup> $J_{CH}$	
C-1	39.1	3.31; 1H d 3.38; 1H d	$^2J_{H(C-1)H(C-1)} = 22.4$		H-3; H-7; H-1'	AB system
C-2	152.9	–	–	2H-1; H-3; H-1'	2H-2'	Quaternary C-atom
C-3	127.7	6.64; 1H s	–		2H-1; H-4; H-1'	
C-3a	145.6	–	–	2H-1	H-5; H-7	Quaternary C-atom
C-4	120.6	7.32; 1H d	$^3J_{H(C-4)H(C-5)} = 7.3$		H-6	
C-5	126.7	7.26; 1H t	$^3J_{H(C-5)H(C-6)} = 7.5$	H-4	H-7	
C-6	124.3	7.14; 1H t	$^3J_{H(C-6)H(C-5)} = 7.5$	H-5; H-7	H-4	
C-7	124.0	7.39; 1H d	$^3J_{H(C-7)H(C-6)} = 7.3$	H-6	H-5	
C-7a	143.7	–	–		H-4; H-6	Quaternary C-atom
C-1'	47.8	4.36; 1H	$^3J_{H(C-1')2H(C-2')} = 7.6$	2H-2'	H-3; 2H-3'	Chiral C-atom
C-2'	34.2	2.50; 1H m	$^3J_{H(C-2')H(C-1')} = 7.6$ $^2J_{H(C-2')H(C-2')} = 12.6$ $^3J_{H(C-2')H(C-3')} = 8.4$ $^3J_{H(C-2')H(C-3')} = 4.8$	H-1'; 2H-3'		Ten signals

TABLE I. Contd.

	2.13; 1H m		${}^3J_{\text{H}(\text{C-2}')\text{H}(\text{C-1}')} = 7.6$				Eight signals
			${}^2J_{\text{H}(\text{C-2}')\text{H}(\text{C-2}')} = 12.6$				
			${}^3J_{\text{H}(\text{C-2}')2\text{H}(\text{C-3}')} = 7.8$				
C-3'	32.2	3.08; 1H m	${}^2J_{\text{H}(\text{C-3}')\text{H}(\text{C-3}')} = 15.7$	2H-2'	H-4'		Eight signals
			${}^3J_{\text{H}(\text{C-3}')\text{H}(\text{C-2}')} = 8.4$				
			${}^3J_{\text{H}(\text{C-3}')\text{H}(\text{C-2}')} = 4.8$				
		2.98; 1H m	${}^2J_{\text{H}(\text{C-3}')\text{H}(\text{C-3}')} = 15.7$				Five signals
			${}^3J_{\text{H}(\text{C-3}')2\text{H}(\text{C-2}')} = 7.8$				
C-3'a	144.3	–	–	2H-3'	H-1'; 2H-2'; 2H-3'; H-5		Quaternary C-atom
C-4'	124.9	7.31; 1H d	${}^3J_{\text{H}(\text{C-4}')\text{H}(\text{C-5}')} = 7.1$	H-5'	H-3' (2.98 ppm)		
C-5'	126.7	7.22; 1H t	${}^3J_{\text{H}(\text{C-5}')\text{H}(\text{C-6}')} = 6.7$	H-4'			
C-6'	127.1	7.18; 1H d	${}^3J_{\text{H}(\text{C-6}')\text{H}(\text{C-5}')} = 6.7$	H-5'; H-7'			H signal coincides with the 7.17 H
C-7'	125.1	7.17; 1H s	${}^3J_{\text{H}(\text{C-7}')\text{H}(\text{C-6}')} = 0$	H-6'	H-5'		H signal coincides with the 7.18 H
C-7'a	146.2	–	–	H-1'; H-7'	2H-2'; 2H-3'; H-4'; H-6'		Quaternary C-atom

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## ИЗВОД

## НМР АНАЛИЗА 2-(2', 3'-ДИХИДРО-1'Н-ИНДЕН-1'-ИЛ)-1Н-ИНДЕНА

ЈОВАН ЈОВАНОВИЋ<sup>1</sup>, МИХАЕЛ СПИТЕЛЕР<sup>2</sup> и ПЕТЕР СПИТЕЛЕР<sup>3</sup>

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<sup>1</sup>H, <sup>13</sup>C и дводимензионална НМР анализа су примењени да би се одредили НМР параметри 2-(2', 3'-дихидро-1'Н-инден-1'-ил)-1Н-индена. Одређена су хемијска померања свих Н- и С-атома, као и одговарајуће константе купловања и дат је потпун НМР распоред. Предсказане мустре четири различита водоникова атома две метилenske групе инденског структурног елемента потпуно су се поклопиле са сложеним мустрима добијеним на НМР спектру. Деривати индена представљају главне компоненте пироли-тичких уља и НМР подаци о њима могу бити корисни у истраживањима околине.

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