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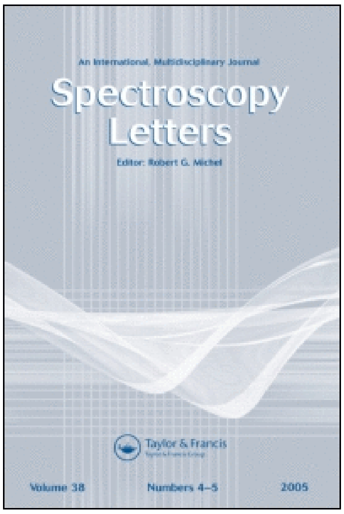

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Structure Elucidation and Assignment of ^{1}H and ^{13}C Spectra of the New Fused Cyclobutane-Naphthofuran Derivative by Two-Dimensional NMR in Different Solvents

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To cite this Article Cvijin, Irena Vujković , Marinić, Željko and Šindler-Kulyk, Marija(1998) 'Structure Elucidation and Assignment of ^{1}H and ^{13}C Spectra of the New Fused Cyclobutane-Naphthofuran Derivative by Two-Dimensional NMR in Different Solvents', Spectroscopy Letters, 31: 5, 989 — 1000

To link to this Article: DOI: 10.1080/00387019808003277

URL: http://dx.doi.org/10.1080/00387019808003277

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SPECTROSCOPY LETTERS, 31(5), 989-1000 (1998)

STRUCTURE ELUCIDATION AND ASSIGNMENT OF ^{1}H AND ^{13}C SPECTRA OF THE NEW FUSED CYCLOBUTANE-NAPHTHOFURAN DERIVATIVE BY TWO-DIMENSIONAL NMR IN DIFFERENT SOLVENTS

Key words: naphtho[2,1-b]furans, cyclobutanes, oxabicyclo[3.2.0]heptenes, ^{1}H NMR, ^{13}C NMR, COSY, LR COSY, NOESY, HETCOR

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ABSTRACT

One of the major product from the photodimerization of 2-[2-(2-methylphenyl)ethenyl)]naphtho[2.1-b]furan (**1**) is a new fused cyclobutane-naphthofuran derivative, 6-(2-methylphenyl)-1-[2-(2-methylphenyl)ethenyl]-7-(2-naphtho-[2,1-b]furyl)-3-[2,1]naphtho-2-oxabicyclo[3.2.0]hept-3-ene (**2**). Its ^{1}H and ^{13}C NMR spectra were fully assigned by the application of COSY, LR COSY, NOESY, APT and HETCOR experiments in deuterated chloroform, acetone and benzene solutions.

INTRODUCTION

Heterocyclic analogs[1,2] of *o*-vinylstilbenes undergo intramolecular photocycloaddition reactions and the formation of bicyclic products. Contrary to these results photocycloaddition of *o*-vinyl-styryl substituted naphthofurans[3] afford a complex mixture of dimeric products in which the vinyl group remained

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unreacted. To facilitate structure determination of the products we irradiated the methyl derivative[3], 2-[2-(2-methylphenyl)ethenyl)]naphtho[2.1-b]furan (**1**) as a model compound. We report herein the structure and the full assignment of ^{1}H and ^{13}C NMR spectra of the dimer **2**. This is the only adduct obtained by intermolecular furan-ethene [2+2] photocycloaddition of **1** (Scheme 1).

Irradiations were performed in benzene solution (10^{-1} M) using a Rayonet reactor equipped with RPR-3500A lamps. The product was isolated in 25% yield from the complex reaction mixture using column and thin layer chromatographies.

RESULTS AND DISCUSSION

There is little spectroscopic information about 2-oxabicyclo[3.2.0]hept-3-ene derivatives[4-6]. To the best of our knowledge this is the first report on the detailed spectroscopic data of such system. Structure determination and assignment of ^{1}H and ^{13}C NMR spectra of the photoproduct **2** is based on different NMR techniques in various solvents.

The dimeric structure of the isolated product **2** was clear from the mass spectrum wich showed an almost inperceivable molecular ion and a basic peak at $M^+/2$ which corresponds to starting compound **1**. The ^{1}H NMR spectrum ($CDCl_3$) showed two methyl groups at 2.27 and 2.77 ppm and a narrow three-proton multiplet at 4.75-4.92 ppm (Fig. 2.c). Three doublets appeared in ^{13}C NMR spectrum at 40.13, 48.99 and 51.76 ppm as well as a singlet at 91.59 ppm. There was also a doublet at 103.41 ppm and 37 carbons in aromatic region. The existence of only three protons in the aliphatic region and only one carbon signal (doublet at 103.41 ppm) in the characteristic region for the furan carbons at the 3 position of the ring revealed an adduct had to be formed by intermolecular [2+2] photocycloaddition of ethene moiety of one molecule with the double bond of furan moiety of the other molecule **1**. This suggests one of two possible structures, A or B (Scheme 2).

It was not possible from the narrow three-proton multiplet in $CDCl_3$ (Fig. 2.c) to choose between two structures, A or B, as well as to determine the relative

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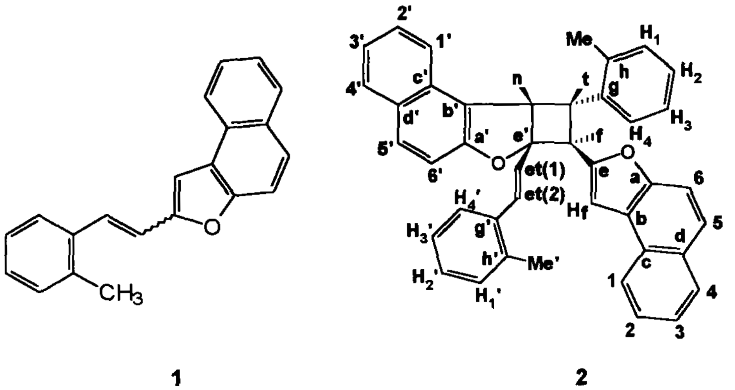
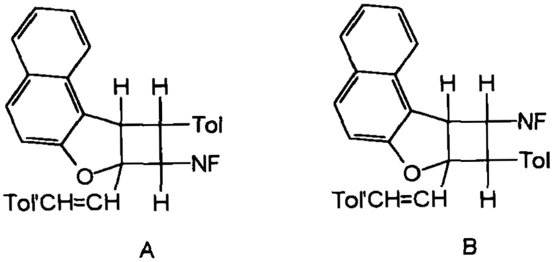


SCHEME 1



SCHEME 2

stereochemistry of the three protons on the fused cyclobutane ring. Therefore the spectra were taken again in deuteroacetone (Fig. 1.b and Fig. 2.b) and deuterobenzene (Fig. 1.a and Fig. 2.a). The three aliphatic protons were best resolved in deuterobenzene (Fig. 2.a) showing three separate signals in the 1:1:1 ratio: a doublet at 5.10 ppm (*J*=11.1 Hz), a doublet of doublets (*J*=11.1 and 8.1 Hz) at 4.87 ppm and a doublet (*J*=8.1 Hz) at 4.74 ppm. From the different vicinal coupling constants of the proton at 4.87 ppm (doublet of doublets) we conclude that the structure has have either cis and trans configuration relative to the other two protons. Thus a structural assignment made on the basis of the magnitude of

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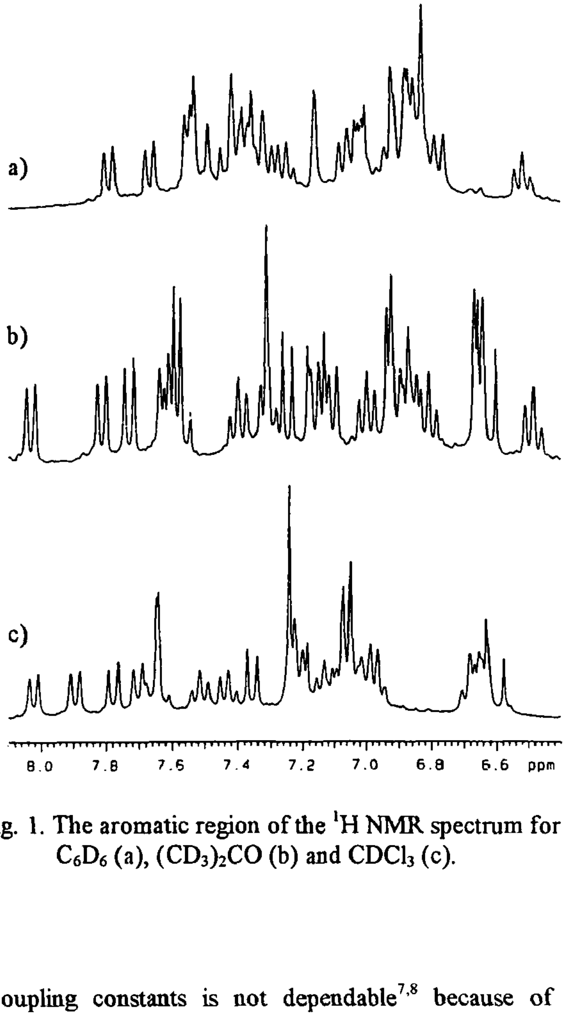

Fig. 1. The aromatic region of the ^{1}H NMR spectrum for **2** in C_6D_6 (a), $(CD_3)_2CO$ (b) and $CDCl_3$ (c).

the vicinal coupling constants is not dependable[7,8] because of their sensitive dependence to the dihedral angle. The coupling values, J_{cis} and J_{trans}, for the vicinal protons on a cyclobutane ring can vary between 3 and 12 Hz[7]. Either cis or trans coupling may be larger depending on the exact conformation of the four-membered ring.[8] Using additional NMR techniques, COSY, LR COSY, NOESY, APT and HETCOR in various deuterated solvents, the structure of the product is clarified completely.

A cross-peak between one methyl group at 2.50 ppm (CH_3) and the cyclobutane proton at 4.87 ppm (doublet of doublets, **t**, Fig.3) in NOESY

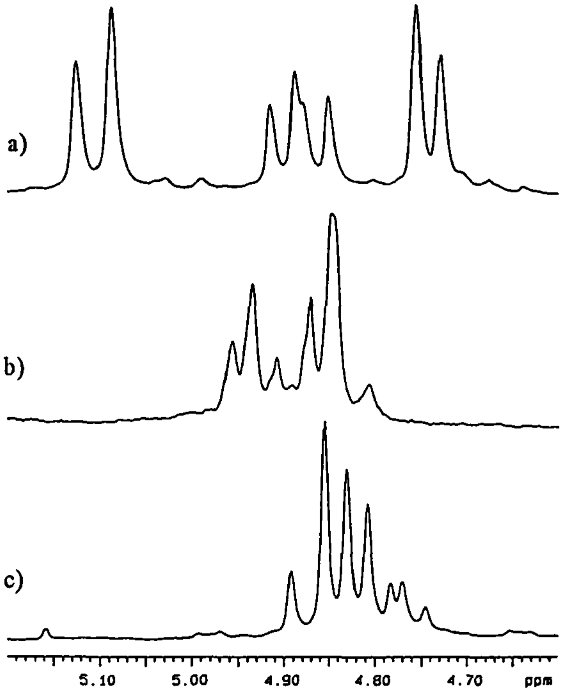

Fig. 2. The aliphatic region of the ^1H NMR spectrum for **2** in C_6D_6 (a), $(CD_3)_2CO$ (b) and $CDCl_3$ (c).

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experiments (C_6D_6, Fig.4) showed that the tolyl group (**Tol**) has to be on the same carbon as the middle hydrogen, i.e. at the position 6 of the 2-oxabicyclo[3.2.0]hept-3-ene ring. This suggests structure A (Scheme 2). Additional cross-peak between the **t** and **n** protons reveal a cis configuration of hydrogens at positions 5 and 6 of the bicyclic ring and, as well, the trans configuration between **t** and **f** protons (Fig. 3,4). The **f** proton showed the large NOE with H_f of the naphthofuran moiety (**NF**). The **n** proton showed a large interaction with the **et(1)** proton in LR COSY and NOESY spectra while the **et(2)** proton showed an interaction with the methyl group at 2.07 ppm (**CH$_3$'**). These data support structure **2** with the styryl group and **n** proton on the same side of the fused cyclobutane ring

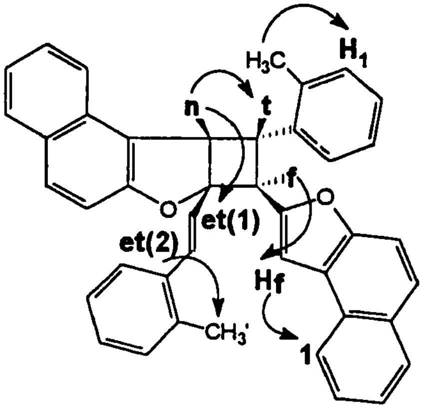

Fig. 3. Important NOESY correlations in compound 2

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as well as the naphthofuryl group. The trans configuration of the double bond of the styryl group was determined from the coupling constant value of the doublet (J=15.9 Hz) that was best resolved in deuterochloroform.

To be able to make these observations, one must correlate the interactions of cyclobutane protons with the corresponding protons in a complex aromatic multiplet, so the complete assignments of all the aromatic protons had to be made. This is achieved by careful examination of the HETCOR spectra in various solvents. Due to the effect the solvent some parts of the aromatic region are better resolved in one solvent than in the other (Figs. 1.a, 1.b, 1.c). The results of combined NMR techniques and complete carbon and proton assignments of the new structure **2** are summarized in Tables 1, 2 and 3.

CONCLUSION

The cyclobutane three protons (**n**, **t** and **f**) were unambiguously assigned and their stereochemical relation determined on the basis of ^{1}H NMR spectrum in C_6D_6 using 2D ^{1}H-^{1}H homonuclear correlation (COSY and LR COSY) and NOE experiments. In the other solvents, $(CD_3)_2CO$ and $CDCl_3$, the same protons

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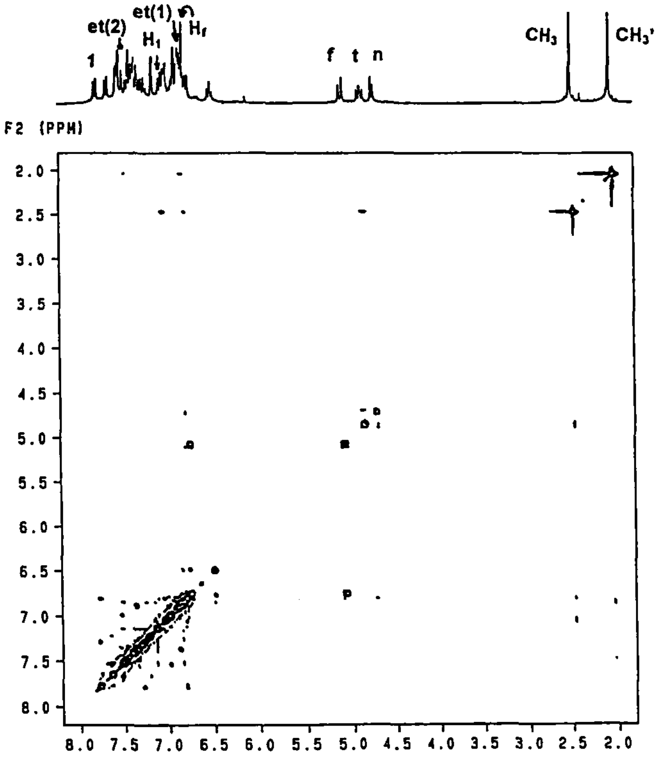

Fig. 4. 2 D NOESY spectrum of compound 2

overlapped and appeared as poorly resoled multiplet. The aromatic protons of the molecule were highly congested in some parts of the spectra, depending on the solvent used. For the full assignment of the ^1H and ^{13}C NMR spectra of the molecule as well as the elucidation of its structure the experiments in various deuterated solvents combining COSY, LR COSY, APT, HETCOR and NOESY techniques were necessary.

EXPERIMENTAL

One- and two-dimensional NMR spectra were recorded on a Varian Gemini 300 spectrometer, operating at 300.1 Mhz for the ^1H and 75.46 MHz for the ^{13}C nuclei,

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TABLE 1
^{1}H and ^{13}C NMR Spectral Data for the Compound 2 in $CDCl_3$

$\delta\,^{13}C$	M[a]	assign.	δ_{attached} H ; J (Hz)	
20.06	q	Me	2.77 s	-
19.56	q	Me'	2.27 s	-
40.13	d	t	4.78 dd	7.5; 11.4
48.99	d	f	4.87 d	11.4
51.76	d	n	4.84 d	7.5
91.59	s	e'	-	-
123.34	d	1	8.02 d	8.1
128.15	d	1'	7.70 d	8.1
126.05	d	2	7.51 t	7.3
122.91	d	2'	7.13 t	7.5
124.28	d	3	7.43 t	7.3
126.05	d	3'	6.99 t	7.5
128.62	d	4	7.89 d	8.1
122.74[c]	d	4'	6.65 d	7.5
124.62	d	5	7.66 d	9.0
130.35	d	5'	7.78 d	9.0
112.18	d	6	7.63 d	9.0
112.92	d	6'	7.36 d	9.0
126.16	d	et(1)	6.60 d	15.9
129.52	d	et(2)	7.21 d	15.9
126.05	d	H_1	7.23 d	7.3
127.69[b]	d	H_1'	7.06 d	7.3
126.86	d	H_2	6.96 t	7.3
130.06	d	H_2'	7.20 t	7.3
125.85[c]	d	H_3	6.65 t	7.3
130.14[b]	d	H_3'	7.01 t	7.3
126.31	d	H_4	6.69 d	7.3
126.05[b]	d	H_4'	7.06 d	7.3
103.41	d	H_f	7.05 s	-
118.73, 123.56	s	b, b'	-	-
152.62, 154.62, 157.91	s	a, a', e	-	-
127.43, 129.29, 130.20, 132.14, 135.57, 135.72, 135.72, 135.78	s	c, d, c', d', g, h, g', h'	-	-

[a] Carbon multiplicities

[b,c] Assignments may be interchanged in each vertical column.

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TABLE 2
^{1}H and ^{13}C NMR Spectral Data for the Compound 2 in $(CD_3)_2CO$

δ^{13}C	M[a]	assign.	δ^{attached}H ; J (Hz)	
19.67	q	Me	2.69 s	-
19.14	q	Me'	2.11 s	-
40.50	d	t	4.89 dd	~6; ~12
49.28	d	f	4.82 d	~12
51.74	d	n	4.93 d	~6
92.17	s	e'	-	-
123.80	d	1	8.03 d	8.1
128.59	d	1'	7.62 d	8.1
126.59	d	2	7.40 ddd	1.5; 7.2; 8.1
123.27	d	2'	7.00 t	7.2
124.80	d	3	7.30 ddd	1.5; 7.2; 8.1
126.39	d	3'	6.87 t	7.2
129.02	d	4	7.81 d	8.1
126.26	d	4'	7.16 d	7.2
125.13	d	5	7.61 d	9.0
130.82	d	5'	7.73 d	9.0
112.39	d	6	7.56 d	9.0
113.15	d	6'	7.25 d	9.0
127.11	d	et(1)	6.63 d	15.6
129.23	d	et(2)	7.15 d	15.6
130.45	d	H_1	7.10 d	7.2
128.06	d	H_1'	6.92 d	7.2
127.11	d	H_2	6.81 t	7.2
126.39	d	H_2'	6.87 t	7.2
125.96	d	H_3	6.48 t	7.2
130.52	d	H_3'	6.92 t	7.2
126.59	d	H_4	6.65 d	8.1
123.33	d	H_4'	6.65 d	8.1
104.06	d	H_f	7.31 s	-
119.38, 124.06,	s	b, b'	-	-
152.93, 155.74, 158.46	s	a, a', e	-	-
127.94, 129.92, 130.77, 132.69, 135.91, 136.23, 136.34, 136.72	s	c, d, c', d', g, h, g', h'	-	-

[a] Carbon multiplicities

TABLE 3

^1H and ^{13}C NMR Spectral Data for the Compound **2** in C_6D_6

$\delta\,^{13}C$	M[a]	assign.	$\delta^{attached}$ H ; *J* (Hz)	
20.30	q	Me	2.50 s	-
19.90	q	Me'	2.07 s	-
41.19	d	t	4.87 dd	8.1; 11.1
50.08	d	f	5.10 d	11.1
52.70	d	n	4.74 d	8.1
92.68	s	e'	-	-
124.22	d	1	7.79 d	8.1
129.12[c]	d	1'	7.53 d	7.8
126.62	d	2	7.29 t	~7
123.71	d	2'	7.03 t	7.8
124.94	d	3	7.25 t	~7
123.66	d	3'	6.81 t	7.8
129.37	d	4	7.66 d	8.1
126.80	d	4'	7.01 d	8.1
125.56	d	5	7.34 d	9.0
131.38[c]	d	5'	7.53 d	8.7
112.72	d	6	7.42 d	9.0
113.62	d	6'	7.39 d	8.7
127.57	d	et(1)	6.83 d	16.2
130.14	d	et(2)	7.50 d	16.2
130.72	d	H_1	7.06 d	7.3
130.92[b]	d	H_1'	6.83 d	
126.89[b]	d	H_2	6.88 t	7.3
128.50	d	H_2'	6.91 t	
126.80	d	H_3	6.51 t	7.3
127.46[b]	d	H_3'	6.85 t	
127.17	d	H_4	6.76 d	7.3
126.89	d	H_4'	7.36 d	
104.37	d	H_f	6.82 s	-
119.82, 124.50	s	b,b'	-	-
153.56, 155.45, 159.09	s	a,a',e	-	-
130.37, 130.60, 130.60, 131.18, 133.31, 136.32, 136.47, 136.70	s	c, d, c', d', g, h, g', h'	-	-

[a] Carbon multiplicities

[b] Assignments may be interchanged in each vertical column

[c] Interchangeable δ values for carbon atoms

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respectively. Spectra were measured in $CDCl_3$, C_6D_6 and $(CD_3)_2CO$ solutions at room temperature using 5 mm diameter NMR tubes. Reference was to the TMS signal. The proton spectrum was recorded using a single 30^0 (6 ms) pulse, 1 s relaxation delay time, with the acquisition time 2 s, and a total sweep width of 3000 Hz sampled with 32 K points. Data processing employed a Lorentz linebroadening factor of 0.5 Hz. The ^{13}C was recorded using a single 45^0 (6 ms) pulse, 1 s relaxation delay time, 0.7 s acquisition time, and a total sweep width of 19000 Hz sampled with 32 K points. Data processing employed a Lorentz linebroadening factor of 1.2 Hz. COSY, LR COSY, NOESY, APT and HETCOR techniques used standard pulse sequences of the Varian Gemini software package. The COSY and LR COSY spectra were obtained in the magnitude mode, whereas NOESY spectra were obtained in the phase-sensitive mode. For COSY, LR COSY and NOESY experiments 1024 points in the F2 dimension and 256 increments in F1 dimension, the latter zero-filled to 1024 points, were used. LR COSY spectra were recorded at the same conditions as COSY spectra using t_3 time delay of 200 ms before acquisition time to emphasize the long range couplings. Each increment in COSY, LR COSY and NOESY experiments was obtained using 16 scans, a relaxation delay of 1 s and a spectral width of 3000 Hz. The mixing time in NOESY experiments was generally set at 0.9 seconds.[9] The HETCOR spectra were measured with 2048 points in F2 dimension and 512 increments in F1 dimension, which were zero filled to 1024 points. Each increment was obtained using 128 scans, a relaxation delay of 1 s and the spectral width of 19000 Hz in F2 and 3000 Hz in F1 dimensions, respectively. The resolution in F2 was 18.6 Hz/point and 5.7 Hz/point in F1 dimension. The protons were decoupled with Waltz-16-modulation.

ACKNOWLEDGMENTS

We thank Prof. D.C.Neckers for critical reading of the manuscript. Financial support from the Ministry of Science and Technology of the Republic of Croatia under contract 125004 is gratefully acknowledged.

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Date Received: February 2, 1998
Date Accepted: March 12, 1998

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