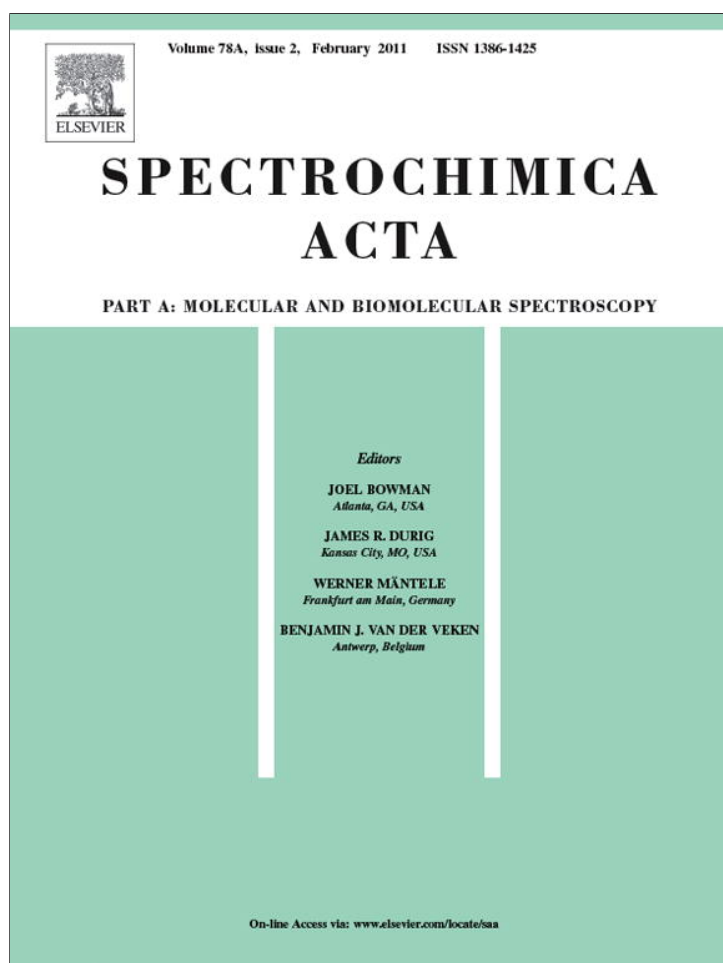


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Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saaA complete ^1H and ^{13}C NMR data assignment for 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-onePlamen N. Penchev^{a,*}, Neyko M. Stoyanov^b, Marin N. Marinov^a^a Department of Chemistry, University of Plovdiv, 4000 Plovdiv, Bulgaria^b University of Rousse, Branch-Razgrad, 7200 Razgrad, Bulgaria

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ABSTRACT

Complete assignments of the ^1H and ^{13}C NMR chemical shifts for 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-one were done by means of one- and two-dimensional NMR techniques, including ^1H - ^1H COSY, HMQC and HMBC spectra. *Ab initio* quantum chemistry calculations and a shift prediction by an incremental method provided values close to the proposed assignments. All mid-IR spectral bands are given as reference data. The DRIFT FTIR, ATR FTIR and Raman spectra are given as a [Supplementary data in JCAMP-DX format, version 4.24](#). In addition, a method of compound's synthesis, that has the product yield higher as compared to already known data in the literature, is given.

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1. Introduction

It is known that 2-aryl-2,3-dihydrophenalene-1,3-diones are compounds which easily isomerize to the respective naphthalides in alkaline environment when exposed to radiation with UV-light, thermally treated at above 200 °C or treated with concentrated hydrobromic acid. In this way they can be obtained as intermediate products related to the synthesis of anticoagulant compounds [1]. It has been established that such compounds have luminescent features and can be used as luminophore markers [2].

For the first time such compound – 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-one – is described in works [3–5]. We should point out that the yields reported are very low and nothing has been said about some characteristic features, only few scarce spectral data has been disclosed. The same product was subsequently obtained at different reaction conditions also by the Wanag's team [6,7]. Later this compound was obtained in order to synthesize a number of new products from the fine organic synthesis [8–11].

The purpose of the current research is to report a spectral investigation of the structure of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-one as the latter appears to be a basic

compound for a further analysis of a number of derivatives which will be subsequently reported. The paper supplies fully-assigned ^1H and ^{13}C NMR spectra together with unassigned FTIR and Raman spectra which will serve as a valuable reference data. In addition, we present a method of synthesis of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-one that has the product yield higher as compared to already known data in the literature.

2. Experimental

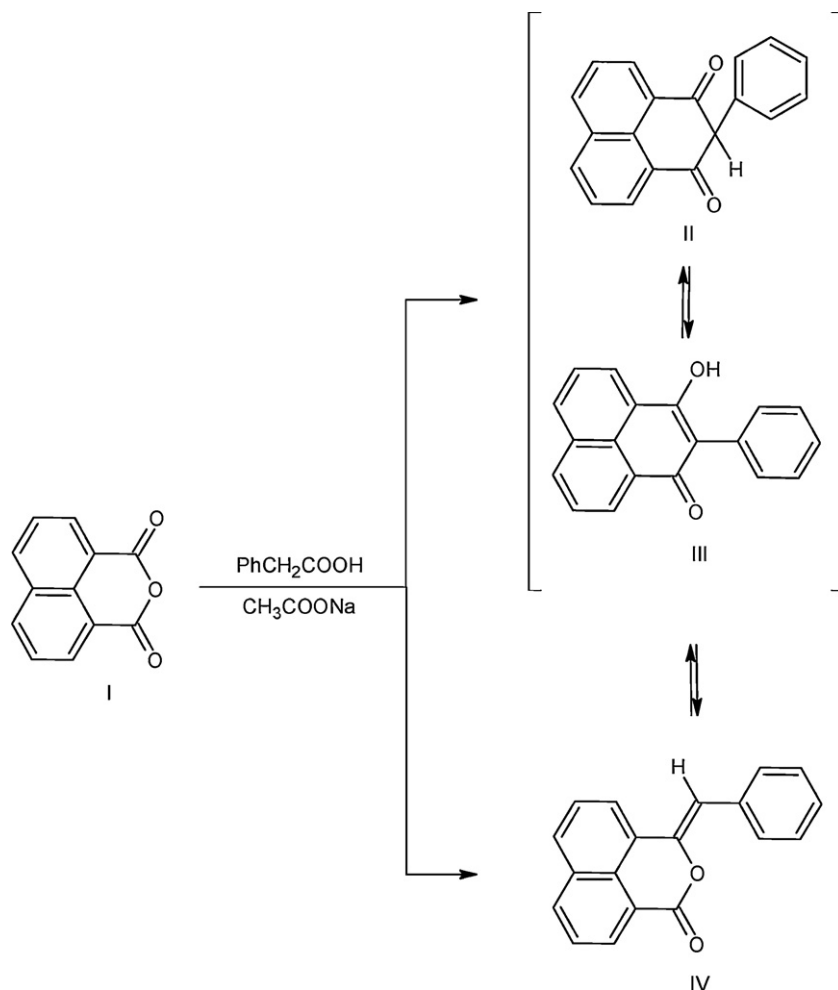
2.1. Synthesis of

3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-one

The synthesis of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*c,d*]-pyran-1-one (**IV**) is performed in accordance with reaction Scheme 1. A mixture of 7.93 g (0.04 mol) 1,8-naphthalic anhydride (**I**), 16.0 g (0.12 mol) phenylacetic acid and 4.8 g (0.06 mol) anhydrous sodium acetate is heated at 240–250 °C for 2 h. It has been experimentally established that when heating is performed for more than 3 h the products (**II**) and (**III**) are predominantly obtained, and for less than 1 h—product **IV**. After completion of heating, the reaction mixture is cooled down to 50–60 °C and 50 ml of ethanol are added to it. The mixture is then cooled down to room temperature and filtered. The solid sediment is dissolved in 3% aqueous ammonia, and the non-dissolved part is separated through filtering and edulcorated with water until a neutral reaction has been obtained. The filtrate is acidified with glacial CH_3COOH till

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Scheme 1.

pH 6.5 during which products **II** and **III** are obtained (with mp 218–219 °C, which is comparable with those in Ref. [6] and Ref. [10]). The solid sediment is extracted with a petroleum ether in a Soxhlet apparatus until product **IV** is isolated. The product obtained is recrystallized from ethanol.

The melting point of **IV** was determined with a Koffler apparatus. The elemental analysis data were obtained with an automatic analyzer Carlo Erba 1106. The product was analyzed for C and H, giving results within $\pm 0.2\%$ of the calculated values.

Yield: 5.7 g (53%).

mp 148–149 °C. (in Ref. [11] 147–148 °C)

Elemental analysis data, anal. calcd. (found)/%: C 83.81 (83.72); H 4.44 (4.38).

$R_{f_a} = 0.63$, $R_{f_b} = 0.77$ (eluent systems: a—EtAc:petroleum ether = 1:2; b— CHCl_3 : CH_3COCH_3 = 9:1).

2.2. Instrumentation and spectral measurements

^1H , ^{13}C and 2D NMR spectra of **IV** were recorded on a Bruker Avance II + 600 MHz NMR spectrometer operating at 600.130 MHz (^1H) and 150.903 MHz (^{13}C), using TMS as internal standard and DMSO-d_6 as solvent. The temperature was kept at 293.0 K for all NMR experiments. Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hertz. 1D and 2D NMR spectra were recorded using the standard Bruker pulse. For ^1H , ^{13}C NMR and 2D NMR spectral data of **IV** see Table 1.

The IR spectrum of **IV** was registered in KBr pellet on a Perkin-Elmer 1750 FT-IR Spectrometer from 4000 cm^{-1} to 450 cm^{-1} at resolution 4 cm^{-1} with 9 scans. A curved baseline correction was performed with the instrument function FLAT to obtain the real band intensities cited below.

The IR spectral bands of **IV**, ν_{max} (cm^{-1})/transmittance (%): 3436/94.7, 3080/88.9, 3056/82.7, 3020/90.5, 1944/95.6, 1895/96.5, 1851/95.5, 1776/95.6, 1730/10.0, 1668/92.2, 1630/73.6, 1597/88.9, 1582/86.5, 1542/95.6, 1514/74.2, 1495/78.4, 1466/89.7, 1449/81.2, 1440/88.1, 1405/85.0, 1372/90.5, 1362/86.5, 1341/69.7, 1306/92.2, 1251/19.3, 1224/72.9, 1184/39.5, 1156/84.2, 1144/56.1, 1123/81.2, 1085/69.1, 1069/49.0, 1032/88.1, 999/95.6, 979/95.6, 930/93.9, 916/82.7, 869/78.4, 861/82.0, 832/71.0, 797/95.6, 767/59.2, 751/46.4, 690/64.8, 660/86.5, 603/95.6, 569/94.7, 533/98.2, 491/71.4.

The Raman spectrum of **IV** (the stirred crystals placed in aluminium disc) was measured on RAM II (Bruker Optics) with a focused laser beam of 50 mW power of Nd:YAG laser (1064 nm) from 4000 cm^{-1} to 51 cm^{-1} at resolution 2 cm^{-1} with 25 scans. Its Diffuse Reflectance FTIR (DRIFT) and Attenuated Total Reflection FTIR (ATR) spectra were recorded with a VERTEX 70 FT-IR spectrometer (Bruker Optics). The used DRIFT accessory is Praying Mantis™ (Harrick Scientific) and crystals of **IV** were stirred with KBr; the spectrum is from 4000 cm^{-1} to 400 cm^{-1} at resolution 2 cm^{-1} with 49 scans. The ATR accessory is MIRacle™ with a one-reflection ZnSe element (Pike) and the stirred crystals of **IV** were pressed by an anvil to the reflection element; the spectrum is from 4500 cm^{-1} to 600 cm^{-1} at resolution 2 cm^{-1} with 16 scans.

Table 1¹H and ¹³C NMR spectral data and ¹H–¹H COSY and HMBC correlations for **IV** [600.13 MHz (¹H) and 150.903 MHz (¹³C)]^a.

Atom	$\delta(^{13}\text{C})$ (ppm)	DEPT ^b	$\delta(^1\text{H})$ (ppm)	Multiplicity (J, Hz)	¹ H– ¹ H COSY ^b	HMBC ^b
1 (C=O)	159.61	C				
3	146.21	C				
4	122.23	CH	8.345	dd(7.8, 0.9)	5, 6 ^c , 1 ^d	3, 6, 9a ^d , 10, 11 ^d
5	127.39	CH	7.741	t(7.8)	4, 6	10a, 11
6	128.32	CH	8.097	d(7.8) ^e	4 ^c , 5	4, 7 ^c , 10, 11 ^c
7	134.43	CH	8.354	dd(8.4, 1.2)	9 ^c , 8	9, 9a ^d , 10, 11 ^d
8	126.86	CH	7.784	dd(8.4, 7.2)	7, 9	9 ^d , 9a, 11
9	129.23	CH	8.330	dd(7.2, 1.2)	7 ^c , 8	1 ^c , 7, 10
9a	119.06	C				
10	127.50	C				
10a	123.70	C				
11	132.00	C				
1'	108.18	CH	7.059	s	4 ^d , 3'/7' ^c	1 ^c , 2' ^c , 3, 10a, 3'/7'
2'	134.13	C				
3'	129.62	CH	7.941	dd(7.8, 1.2)	4', 5' ^c , 1' ^c	1', 5', 7'
4'	128.55	CH	7.466	t(7.8)	3', 5'	2', 6'
5'	127.53	CH	7.326	tt(7.8, 1.2)	4'/6', 3'/7' ^c	3'/7'
6'	128.55	CH	7.466	t(7.8)	7', 5'	2', 4'
7'	129.62	CH	7.941	dd(7.8, 1.2)	6', 5' ^c , 1' ^c	1', 3', 5'

^a In DMSO-d₆ solution. All these assignments were in agreement with COSY, HMQC^b and HMBC spectra.^b Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ¹H–¹H COSY–proton–proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, long range ¹H–¹³C Heteronuclear Multiple Bond Correlation experiment.^c These correlations are weak.^d These correlations are extremely weak.^e ¹H signal of H-6 is doublet with widened signals instead of doublet of doublets.

Those three types of spectra are given as a [Supplementary data in JCAMP-DX format, version 4.24](#).

3. Computational details

To additionally verify the proposed assignments, quantum chemistry calculations were performed by using the Gaussian 98, Revision A.7 [12]. For the geometry optimization the B3LYP density functional with 6-31G(d) basis set was used and for the ¹H and ¹³C NMR spectra prediction the HF/6-31G(d) calculations were carried out at the optimized geometry.

4. Results and discussion

Compound **IV** has the molecular formula C₁₉H₁₂O₂. Its structure and the numbering of the atoms (which is only for spectral assignments) are given in Fig. 1; the structure of **IV** is only illustrative and the relevant configuration of the exocyclic double bond (Z or E) is not a subject of the present paper. The ¹³C NMR spectrum of **IV** showed 17 signals (atoms 3' and 7' as well as 4' and 6' are magnetically equivalent) and DEPT displayed 10 resonances for CH. The high intensity (nearly double intensity compared to the others) of the resonances at 129.62 ppm and 128.55 suggests that each of them corresponds to two carbon atoms; the signal at 129.62 ppm is for C-3'/7' and that at 128.55 is for C-4'/6'. The signal with the highest chemical shift in ¹³C NMR spectrum, 159.61 ppm, is for the carbonyl group (atom 1), and that with the lowest one, 108.18 ppm, for olefin CH carbon (atom 1'). The signal at 146.21 ppm is assigned to the other olefin carbon, atom 3. These five assignments are confirmed by the 2D spectra (see "discussion" that follows).

The ¹H NMR spectrum of **IV** is presented in Fig. 2; there appear eight groups of multiplet—the multiplet at δ 8.36–8.32 ppm is with integral of 3.0. The multiplets at 7.941 ppm and 7.466 ppm with integral of 2.0 are for the protons in phenyl ring (atoms 3'/7' and 4'/6'). Heteronuclear Multiple Quantum Correlation experiment (HMQC) was used to assign proton signals to the corresponding carbon signals; the ten HMQC correlations are well separated—see Fig. 3. Three of the ten HMQC correlations correspond to the multiplet at δ 8.36–8.32 ppm in ¹H spectrum (with integral of 3.0) that is why it is composed of three signals. This

group of ¹H signals is modeled by curve-fitting with three doublets of doublets with $\delta_1(7) = 8.354$ ppm, $^3J_1 = 8.4$ Hz, $^4J_1 = 1.2$ Hz, $\delta_2(4) = 8.345$ ppm, $^3J_2 = 7.8$ Hz, $^4J_2 = 0.9$ Hz and $\delta_3(9) = 8.330$ ppm, $^3J_3 = 7.2$ Hz, $^4J_3 = 1.2$ Hz (subscript at δ corresponds to the numbering of signals from high to low shift and in the parentheses is given the atom numbering from Fig. 1). They are finally assigned to protons at atoms 7, 4 and 9 (see the discussion that follows). There are strong ¹H–¹H COSY correlations (see Table 1 and Fig. 4) between $\delta_1(7) = 8.354$ ppm and $\delta_6(8) = 7.784$ ppm, and $\delta_3(9) = 8.330$ ppm and $\delta_6(8) = 7.784$ ppm, and a weak one between $\delta_1(7) = 8.354$ ppm and $\delta_3(9) = 8.330$ ppm. Since $\delta_3(9) = 8.330$ ppm shows a weak HMBC correlation (see Table 1 and Fig. 5) to 159.61 ppm (¹³C signal of the carbonyl group), the former signal is assigned to the proton at atom 9, while $\delta_1(7) = 8.354$ is assigned to H-7, and $\delta_6(8) = 7.784$ ppm to H-8.

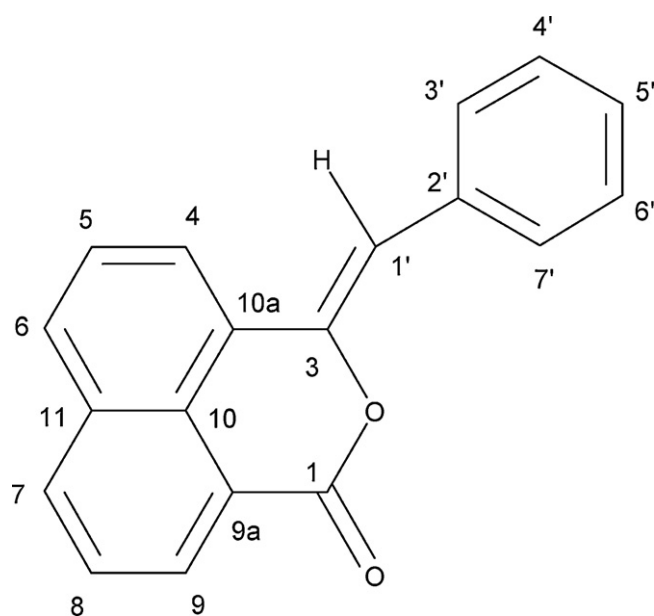


Fig. 1. Structure of 3-Phenylmethylene-1H,3H-naphtho-[1,8-c,d]-pyran-1-one **1**. The numbering of the atoms is only for spectral assignments.

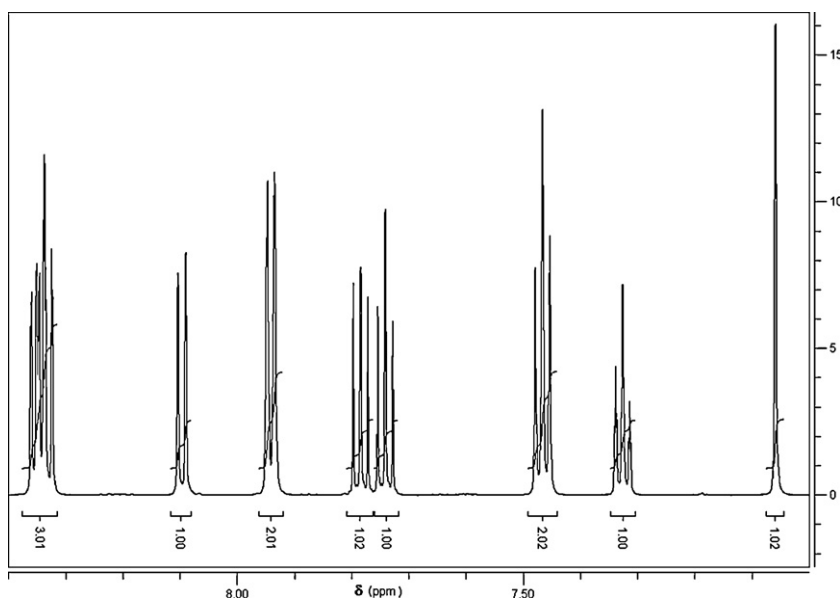


Fig. 2. ^1H NMR spectrum of IV. The integrals of the signals are shown at the bottom of the multiplets.

On the other side, there are strong ^1H - ^1H COSY correlations between $\delta_2(4)=8.345$ ppm and $\delta_7(5)=7.741$ ppm, and $\delta_4(6)=8.097$ ppm and $\delta_7(5)=7.741$ ppm, and a weak one between $\delta_2(4)=8.345$ ppm and $\delta_4(6)=8.097$ ppm. Since $\delta_2(4)=8.345$ ppm shows strong HMBC correlation to 146.21 ppm (^{13}C signal of olefin carbon next to the oxygen), the former signal is assigned to the proton at atom 4, while $\delta_4(6)=8.097$ ppm is assigned to H-6, and $\delta_7(5)=7.741$ ppm to H-5. This six assignments made for proton signals ($\delta\#$ 1, 2, 3, 4, 6 and 7 to atom# 7, 4, 9, 6, 8 and 5 of the naphthalene moiety) are additionally supported by the coupling constants and multiplet structure of the discussed signals—see Multiplicity column of Table 1. The only exception is the doublet at 8.097 (proton at atom 6) which has to be doublet of doublets but the weak coupling ($^4J=0.9$ Hz) does not split the doublet and only widens its signals.

The assignment of $\delta_5(3'/7')=7.941$ ppm, $\delta_8(4'/6')=7.466$ ppm and $\delta_9(5')=7.326$ ppm to the phenyl protons H-3'/7', H-4'/6' and H5' is straightforward and is confirmed by ^1H - ^1H COSY and the structure and integrals of the corresponding multiplets. As can be seen from Fig. 4, the proton at 3' shows a strong correlation with the neighboring proton at 4' (respectively that at 7' with that at 6') and both protons (at 3' and 7') have a weak one with the proton at 5', giving doublet of doublets for $\delta_5(3'/7')$. The same correlations and the correlation of the protons at 4' and 6' with the proton at 5' determine the triplet structure of the signal for the protons at 4' and 6'. The signal $\delta_9(5')$ is a triplet of triplets by reason of the correlations mentioned above. Additionally, there exists a weak correlation between the proton at 1' and the protons at 3' and 7'; this confirms that the proton at 1' is a neighbor of those at 3' and 7'.

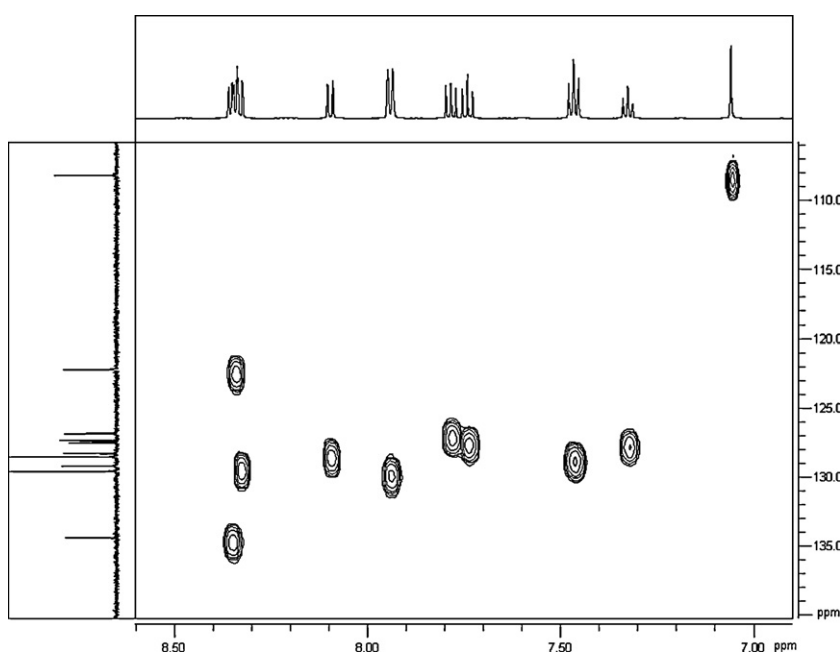


Fig. 3. Detail of the HMQC spectrum of IV. 1D trace (left) is ^{13}C DEPT-135 NMR spectrum and 1D trace (top) is ^1H NMR spectrum.

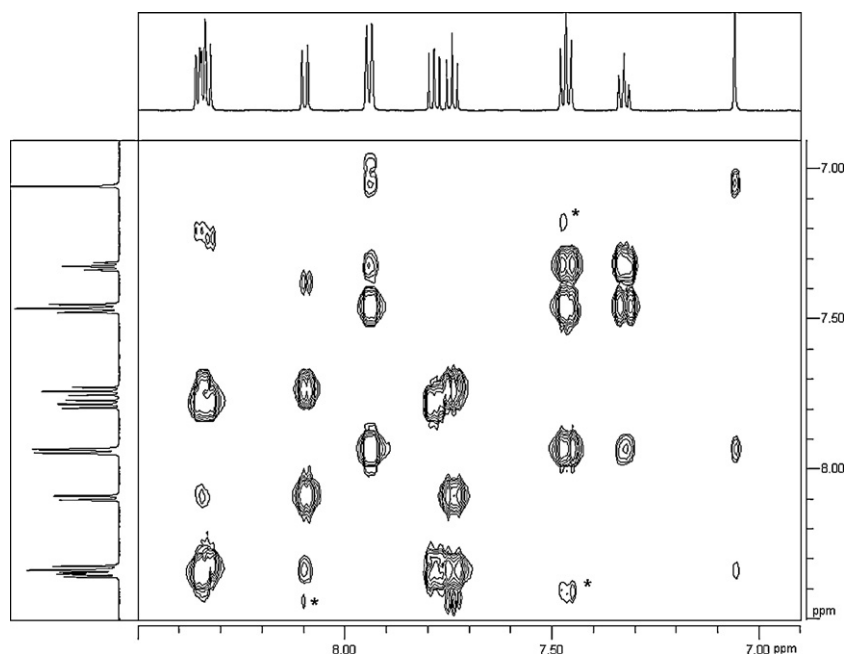


Fig. 4. Detail of the COSY spectrum of IV. Both 1D traces (top and left) are ^1H NMR spectrum of the compound. Three signals marked with * are noise.

As nearly half of ^{13}C signals build groups with a close shift, the analysis of HMBC correlations appeared to be more complex. First, for the CH coupling in benzene rings, as described in the literature [13], only the meta (vicinal) coupling ($^3J_{\text{CH}}$) is usually resolved. The measured HMBC correlations (see Table 1 and Fig. 5) confirmed that definitely: for naphthalene moiety the strong couplings are $\text{H}_4\text{--C}_6$, $\text{H}_4\text{--C}_{10}$, $\text{H}_5\text{--C}_{10a}$, $\text{H}_5\text{--C}_{11}$, $\text{H}_6\text{--C}_4$, $\text{H}_6\text{--C}_{10}$, $\text{H}_7\text{--C}_9$, $\text{H}_7\text{--C}_{10}$, $\text{H}_8\text{--C}_{9a}$, $\text{H}_8\text{--C}_{11}$, $\text{H}_9\text{--C}_7$, $\text{H}_9\text{--C}_{10}$ and for the phenyl ring $\text{H}_{3'/7'}\text{--C}_{5'}$, $\text{H}_{3'}\text{--C}_{7'}$, $\text{H}_{4'/6'}\text{--C}_{2'}$, $\text{H}_{4'}\text{--C}_{6'}$, $\text{H}_{5'}\text{--C}_{3'/7'}$, $\text{H}_{6'}\text{--C}_{4'}$, $\text{H}_{7'}\text{--C}_{3'}$.

Second, there is an HMBC correlation between $\delta_{10} = 7.059$ ppm (signal of $\text{H-1}'$) and ^{13}C signal at 134.13 ppm (not present in DEPT) that is why the latter was assigned to carbon 2'; this assignment is also confirmed by the above mentioned HMBC correlations

in the phenyl ring. The signals $\delta_{10}(\text{H-1}') = 7.059$ ppm and $\delta_2(\text{H-4}) = 8.345$ ppm show strong HMBC correlations with 146.21 ppm which confirmed the assignment of the latter signal to the olefin carbon next to the oxygen (C-3). There is also a strong HMBC correlation between $\delta_{10} = 7.059$ ppm ($\text{H-1}'$) and ^{13}C signal at 123.70 ppm (C-10a) which additionally confirmed the assignment of the latter.

Third, there is a strong HMBC correlation between $\delta_5 = 7.941$ ppm ($\text{H-3}'/7'$) and ^{13}C signal at 108.18 ppm (C-1') and a strong one between $\delta_{10} = 7.059$ ppm ($\text{H-1}'$) and ^{13}C signal at 129.62 ppm (C-3'/7'), which is in accordance with the assignment of proton signals with integral of two $\delta_5 = 7.941$ ppm and $\delta_8 = 7.466$ ppm to $\text{H-3}'/7'$ and $\text{H-4}'/6'$.

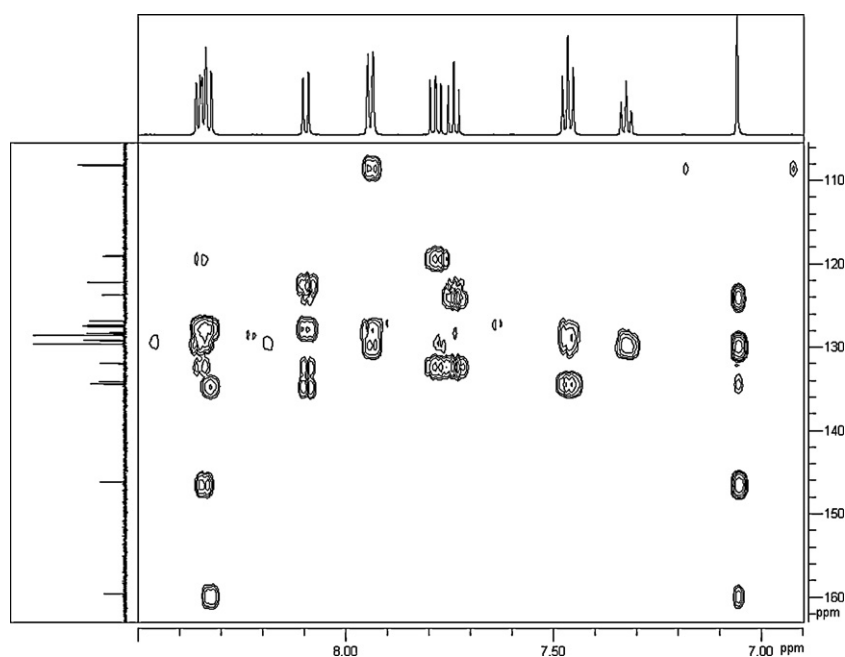


Fig. 5. Detail of the HMBC spectrum of IV. 1D trace (left) is ^{13}C NMR spectrum and 1D trace (top) is ^1H NMR spectrum.

Table 2
Calculated ^1H and ^{13}C NMR spectral data for **IV**.

Atom	$\delta(^{13}\text{C})$, exp ^a (ppm)	$\delta(^{13}\text{C})$, calc by QC ^a (ppm)	$\delta(^{13}\text{C})$, calc by ChemDraw ^a (ppm)	$\delta(^1\text{H})$, exp ^a (ppm)	$\delta(^1\text{H})$, calc by QC ^a (ppm)	$\delta(^1\text{H})$, calc by ChemDraw ^a (ppm)
1	159.61	159.33	163.0			
3	146.21	142.52	143.2			
4	122.23	122.55	124.0	8.345	8.424	7.82
5	127.39	124.82	124.5	7.741	7.876	7.57
6	128.32	127.99	127.4	8.097	8.139	7.76
7	134.43	135.50	132.8	8.354	8.442	8.09
8	126.86	123.21	123.2	7.784	7.860	7.55
9	129.23	135.40	129.5	8.330	9.180	8.43
9a	119.06	117.69	122.2			
10	127.50	130.17	127.7			
10a	123.70	124.70	132.3			
11	132.00	130.03	134.2			
1'	108.18	109.61	98.1	7.059	6.630	6.41
2'	134.13	132.87	134.9			
3'	129.62	130.94 ^b	126.2	7.941	8.459 ^d	7.42
4'	128.55	126.94 ^c	128.4	7.466	7.655 ^e	7.26
5'	127.53	127.72	127.7	7.326	7.557	7.11
6'	128.55	126.94 ^c	128.4	7.466	7.655 ^e	7.26
7'	129.62	130.94 ^b	126.2	7.941	8.459 ^d	7.42

^a Abbreviations: exp, experimental value; calcd. by QC, value calculated with quantum chemistry (for the used method see the text); calcd. by ChemDraw, value calculated with the incremental method of ChemDraw Ultra.

^b Average between 131.30 ppm and 130.57 ppm.

^c Average between 127.86 ppm and 126.01 ppm.

^d Average between 9.458 ppm and 7.461 ppm.

^e Average between 7.762 ppm and 7.548 ppm.

A full set of ^1H and ^{13}C NMR assigned spectral data for the compound **IV** is shown in the Table 1 together with 2D data; the strength of 2D correlations is given also (see footnotes c and d in Table 1).

There are four aromatic carbons in the naphthalene moiety of the compound **IV** without protons: 9a, 10, 10a and 11. As described above, their assignments are entirely based on the present strong meta (vicinal) HMBC couplings and the strong HMBC correlation between H-1' and C-10a. It was expected that some shift predictions can confirm our assignments.

The predicted chemical shifts by quantum chemistry calculations are given in Table 2 together with those predicted by the incremental method implemented in ChemDraw Ultra 7.0.4 [14]. The ^{13}C shift predictions made by quantum chemistry have a standard error of 2.3 ppm with a maximum deviation of 6.17 ppm (for carbon 9) and those for ^1H shift have a standard error of 0.37 ppm with a maximum deviation of 0.85 ppm (for proton at carbon 9). The incremental method's predictions have a standard error of 3.4 ppm with a maximum deviation of 10.08 ppm (for carbon 1') and those for ^1H shift have a standard error of 0.37 ppm with a maximum deviation of 0.65 ppm (for proton at carbon 1'). As seen from Table 2, the quantum chemistry predictions for C-10 and C-11, 130.17 ppm and 130.03 ppm are very close one another and differ by more than 1.95 ppm from the assigned shift values. On the other side, the incremental predictions for these two carbons are in good agreement with the proposed assignments; only the predicted shift for C-10a, 132.3 ppm, differs significantly from the assigned value of 123.70 ppm. The shift for C-10a, 124.70 ppm, is predicted by quantum chemistry and as mentioned above, this assignment is confirmed by a strong HMBC correlation between H-1' and C-10a.

5. Summary and conclusions

The ^1H , ^{13}C and 2D NMR spectra of 3-phenylmethylene-1H,3H-naphtho-[1,8-c,d]-pyran-1-one including ^1H - ^1H COSY, HMQC and HMBC spectra have been recorded and analyzed. The complete assignments of the ^1H and ^{13}C NMR chemical shifts have been proposed. Density functional theory calculations at the B3LYP/6-31G(d) level have been used for geometry optimization and HF/6-31G(d) calculations have been applied to compute the chem-

ical ^1H and ^{13}C shifts. These calculations and a shift prediction by an incremental method provided shift values close to the proposed assignments.

The mid-IR, DRIFT FTIR, ATR FTIR and Raman spectra of 3-phenylmethylene-1H,3H-naphtho-[1,8-c,d]-pyran-1-one were recorded. All mid-IR spectral bands are given as reference data and the other vibrational spectra are attached as Supplementary data in JCAMP-DX format, version 4.24.

In addition, a method of synthesis of a 3-phenylmethylene-1H,3H-naphtho-[1,8-c,d]-pyran-1-one is described; that method has the product yield higher as compared to already known data in the literature.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.11.015.

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