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Spectral Assignments and Reference Data

NMR spectroscopic data of some 1-alkoxy-2,2-di(carbonyl, carboxyl, cyano)-substituted ethylenes†

Christian Hametner,[1]* Petra Černuchová,[2] Viktor Milata,[2] Giang Vo-Thanh[3] and André Loupy[3]

[1] Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria
[2] Department of Organic Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic
[3] Institute of Molecular Chemistry, CNRS UMR 8615, University Paris-South, Orsay F-914 05, France

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The ^{1}H–^{13}C NMR shifts as well as ^{1}H and ^{13}C coupling constants of 14 alkoxymethylene malonic acid and acetoacetic acid derivatives and two alkoxymethylene acetylacetones are reported. The ^{17}O NMR spectra have been recorded for six of them. The long-range coupling $^3J(\mathrm{H—C{=}C—C^R})$ has been used for determining the stereochemistry of the double bond. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; ^{17}O NMR; ^{1}H and ^{13}C coupling constants; alkoxymethylene malonic acid derivatives; alkoxymethylene acetoacetic acid derivatives; alkoxymethylene acetylacetones; enol ether; *E*/*Z* isomerism

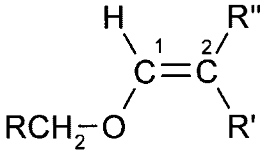
INTRODUCTION

Esters and nitriles of alkoxymethylene malonic acid and acetoacetic acid as well as alkoxymethylene acetylacetones represent a special group of trifunctional enol ethers. Their high reactivity and easy availability render them widely used building blocks in the synthesis of carbocyclic as well as heterocyclic compounds.[1]

Although some spectral data have been published together with their syntheses, so far no review of the spectroscopic properties of this class of molecules has appeared in the literature (however, data collections of related compound types are available[2,3]). Thus, having in hand two sets of methoxymethylene (**1a**—**8a**) and ethoxymethylene (**1b**—**8b**) derivatives of these substances from various synthetic projects (Scheme 1 and Table 1), we prepared a systematic survey of their ^{1}H, ^{13}C and ^{17}O NMR shifts as well as the ^{1}H–^{13}C coupling constants.

EXPERIMENTAL

The title compounds **1**–**8** have been synthesized by condensation of trimethyl or triethyl orthoformate, respectively, with the appropriate active methylene component in the presence of acetic anhydride.



Scheme 1. Structure of compounds studied.

Table 1. List of compounds

Compound	R	R′	R″
1a	H–	–CN	–CN
1b	CH_3–	–CN	–CN
2a	H–	–CN	–$COCH_3$
2b	CH_3–	–CN	–$COCH_3$
3a	H–	–$COCH_3$	–$COCH_3$
3b	CH_3–	–$COCH_3$	–$COCH_3$
4a	H–	–CN	–$COOCH_3$
4b	CH_3–	–CN	–$COOCH_3$
5a	H–	–$COOCH_3$	–$COOCH_3$
5b	CH_3–	–$COOCH_3$	–$COOCH_3$
6a	H–	–CN	–$COOC_2H_5$
6b	CH_3–	–CN	–$COOC_2H_5$
7a	H–	–$COOC_2H_5$	–$COOC_2H_5$
7b	CH_3–	–$COOC_2H_5$	–$COOC_2H_5$
8a	H–	–$COOC(CH_3)_2OCO$–	
8b	CH_3–	–$COOC(CH_3)_2OCO$–	

Table 2. The ^{1}H chemical shifts (ppm, relative to TMS)

Compound	H-1	R	R′	R″
1a	7.63	4.13		
1b	7.69	4.37, 1.40		
2a	7.93	4.13		2.38
2b	7.97	4.28, 1.28		2.16
3a	7.43	3.87	2.17	2.10
3b	7.59	4.15, 1.28	2.25	2.17
4a	7.92	4.06		3.70
4b	7.99	4.32, 1.37		3.73
5a	7.41	3.81	3.59	3.55
5b	7.47	4.02, 1.17	3.57	3.52
6a	7.91	4.06		4.17, 1.23
6b	8.00	4.34, 1.42		4.25, 1.30
7a	7.38	3.83	4.11, 1.16	4.05, 1.13
7b	7.48	4.06, 1.24	4.13, 1.17	4.07, 1.14
8a	8.10	4.21	1.62	
8b	8.14	4.42, 1.38	1.56	

The physical properties were in good agreement with previously described data: **1a**,[4] **1b**,[5] **2a** (not yet published), **2b**,[6] **3a**,[7] **3b**,[8] **4a**,[9] **4b**,[9] **5a**,[7] **5b**,[10] **6a**,[9] **6b**,[9] **7a**,[11] **7b**,[12] **8a**[13] and **8b**.[6]

All spectra were recorded on a Bruker Avance DRX 400 spectrometer controlled by a Silicon Graphics O2 workstation. Using a 5 mm inverse broadband probe-head, spectra were acquired from solutions of ~100–150 mg ml^{-1} in $CDCl_3$. The ^{1}H and ^{13}C spectra were recorded at 300 K and referenced to tetramethylsilane (TMS).

The ^{1}H NMR spectra (400.13 MHz) were recorded using a 30° pulse angle, 4.8 kHz spectral width, pulse repetition time of 4.5 s, 32 k data points and 16 scans. The ^{1}H COSY, ^{1}H-^{13}C HMQC and HMBC spectra were recorded with 2 k data points and 4–8 scans for each FID and 256 increments.

Instrumental settings for CPD-decoupled ^{13}C NMR spectra (100.62 MHz) were: 30° pulse angle, 25.1 kHz spectral width, pulse repetition time 2.3 s, 64 k data points and up to 1000 scans. Exponential multiplication (1 Hz) was applied. For gated decoupled ^{13}C

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†Dedicated to Professor Peter Stanetty on the occasion of his 60th birthday.

*Correspondence to: Christian Hametner, Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria. E-mail: christian.hametner@tuwien.ac.at

NMR spectra 128 k data points were recorded with a pulse repetition time of 3.6 s, followed by zero-filling to 256 k. No exponential multiplication was used and 2000–4000 scans were necessary.

The ^{17}O NMR spectra (54.26 MHz) were acquired at 313 K with a 90° pulse angle, 43.5 kHz spectral width, prescan delay of 40 µs, a pulse repetition time of 0.15 s and 4 k data points. Linear prediction backward was used to overcome rolling baseline problems, recalculating the first 8–16 data points from the following 256 points using 128 filter coefficients. Exponential multiplication (50–100 Hz) was applied and the shifts were referenced to H_2O.

Table 3. The ^{13}C chemical shifts (ppm, relative to TMS)

Compound	C-1	C-2	R	R′	R″
1a	175.83	66.44	64.93	109.73	111.77
1b	174.66	66.00	74.90, 14.74	109.88	111.99
2a	173.04	94.75	64.25	114.11	191.41, 28.05
2b	172.38	94.73	73.73, 14.66	113.67	191.07, 26.82
3a	166.46	121.96	63.24	197.60, 31.59	196.37, 28.47
3b	165.76	121.76	72.80, 14.95	197.61, 31.78	196.87, 28.95
4a	173.78	85.70	64.11	112.33	173.78, 52.07
4b	172.44	85.76	73.80, 14.92	112.54	172.44, 52.18
5a	165.11	105.07	62.80	163.64, 51.34[a]	164.44, 51.16[a]
5b	163.86	104.87	71.97, 14.62	163.74, 51.25[a]	164.60, 51.08[a]
6a	173.46	86.31	64.03	112.41	162.45, 61.37, 13.81
6b	172.27	85.99	73.65, 14.85	112.55	162.61, 61.23, 13.80
7a	164.28	106.18	62.73	163.45, 60.43, 13.68[a]	164.21, 60.18, 13.75[a]
7b	163.21	105.95	71.90, 14.83	163.63, 60.38, 13.72[a]	164.47, 60.17, 13.81[a]
8a	175.04	96.42	66.09	162.85, 158.33[b], 104.40, 26.95	
8b	173.84	96.07	75.92, 14.97	163.03, 158.28[b], 104.22, 26.90	

[a] Assignments may be interchanged.

[b] *Cis* relative to RCH_2O—.

Table 4. The ^{1}H–^{13}C coupling constants (Hz)

Compound	^1J [H-1, C-1]	^2J [H-1, C-2]	^3J [H-1, C(R′)]	^3J [H-1, C(R″)]	^3J [H-1, OCH_2]	^3J [OCH_2, C-1]
1a	186.8	11.6	10.0	3.9	5.8	5.2
1b	185.8	11.6	10.1	4.0	5.6	4.6
2a	183.9	10.2	10.0	2.6	6.2	5.1
2b	182.9	10.8	10.0	2.6	5.8	4.5
3a	179.7	6.1	7.7	3.3	6.6	5.3
3b	178.8	6.0	7.7	3.2	6.4	4.6
4a	185.2	10.0	9.8	2.8	6.2	5.2
4b	183.7	10.0	9.9	2.8	6.0	4.6
5a	181.8	6.9	9.1	3.6	6.5	5.3
5b	180.5	6.8	9.1	3.8	6.3	4.7
6a	185.0	9.9	9.9	2.8	6.2	5.2
6b	183.8	9.8	9.9	2.9	5.9	4.5
7a	181.5	6.7	9.0	3.3	6.5	5.3
7b	180.3	6.7	9.1	3.3	6.3	4.7
8a	181.2	7.2	8.9	3.3	6.9	5.3
8b	179.9	7.2	8.9	3.3	6.6	4.9

Table 5. The ^{17}O chemical shifts (ppm, relative to H_2O) and line widths (Hz)

Compound	RO—CH=CR$_2$	R′, R″
1a	105.8 (280)	—
1b	140.4 (450)	—
3a	84.2 (490)	566.9 (510), 518.6 (530)
3b	116.9 (630)	564.6 (560), 516.2 (570)
4a	101.1 (540)	321.4 (560), 130.5 (680)
6b	130.4 (560)	318.9 (640), 157.9 (570)

RESULTS AND DISCUSSION

A full characterization of $^{1}H-^{13}C$ shifts as well as $^{1}H-^{13}C$ coupling constants was carried out for compounds **1**–**8**. Where not obvious, the assignments are based primarily on the heteronuclear couplings (Table 4); for some compounds with identical R′ and R″ residues additional two-dimensional experiments were necessary (COSY, HMQC, HMBC). Thus, all resonances were completely assigned (Tables 2 and 3), except for the ester groups of compounds **5** and **7**, where the shift differences are too small to differentiate between the carbon atoms of the respective CH_3 groups.

The data in Tables 2–4 show that the effects that nitrile groups exert on the spectroscopic properties of surrounding atoms are pronouncedly different to those of carbonyl and carboxyl residues. This is especially remarkable for the shifts of the olefinic carbon atoms (to the low field for C-1 and the contrary for C-2), but also the increase of the heteronuclear coupling constants within the double bond (^{1}J [H-1, C-1], ^{2}J [H-1, C-2] and to a smaller extent ^{3}J [H-1, C(R′)]) is significant. The effect of the various —CO—groups is much smaller, except for the ring-closed compounds **8**, the properties of which deviate from those of the open-ring esters in a way analogous to the nitriles.

Special attention was paid to the long-range coupling between H-1 and the CO or CN carbon atoms of R′ and R″ as a means of determining the stereochemistry of the double bond. Because the dihedral angle is the most important factor influencing the magnitude of a ^{3}JC,H (although there is some effect of the nature of the coupling carbon atom and the electronic properties of the substituents),[14] the fixed angles of ∼0° and ∼180° in olefinic structures make this coupling a useful tool in the differentiation between geometric isomers.

Indeed, analysis of the respective coupling constants in compounds **1, 3, 5, 7** and **8** (those having identical R′ and R″) showed clearly separated ranges for a *cis* (3.2–4.0 Hz) and a *trans* (7.7–10.1 Hz) coupling path. Thus, the mixed-substituted compounds **2, 4** and **6** could be identified unambiguously as *E* isomers by coupling constants of <3 Hz for the *cis* and ∼10 Hz for the *trans* relation.

Because the measurement of this nucleus is very time consuming, ^{17}O NMR spectra were recorded for only six of the title compounds (Table 5). The shift of the enol oxygen atom is mainly determined by the alkoxy residue (∼30 ppm difference between comparable methoxy and ethoxy derivatives), whereas the influence of the nature of R′ and R″ is less marked.

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