

Infrared Spectra and Theoretical Study of the Conformations of Substituted Benzoylketene-S,S-acetals

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Summary. The C=O stretching frequencies of substituted benzoylketene-S,S-dimethylacetals (**1a–1o**) and benzoylketene-S,S-ethyleneacetals (**2a–2m**) were measured in CHCl₃ and CCl₄ and correlated with the *Hammett* substituent constants. The correlations were split into two different and well separated lines for compounds containing electron donor and electron acceptor substituents, which were assigned to *s-trans* and *s-cis* quasiplanar conformations. The correlations of carbonyl stretching frequencies with C=O bond orders and oxygen atom charge densities calculated using the semi-empirical AM1 method reveal similar results consistent with assignments of structures **1** and **2** to two quasiplanar conformations. The preparation of some new benzoylketene-S,S-acetals is reported as well.

Keywords. Substituted Benzoylketene-S,S-acetals; Infrared Spectra; Conformation; AM1 Calculations.

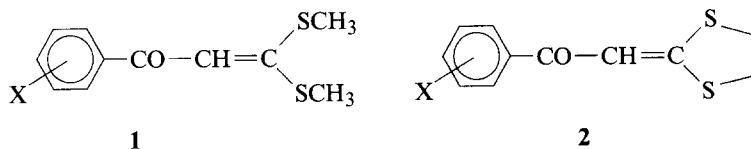
Infrarotspektroskopische und theoretische Untersuchung der Konformationen substituierter Benzoylketen-S,S-acetale

Zusammenfassung. Die C=O-Streckfrequenzen substituierter Benzoylketen-S,S-dimethylacetale (**1a–1o**) und Benzoylketen-S,S-ethylenacetale (**2a–2m**) wurden in CHCl₃ und CCl₄ gemessen und mit den *Hammett*-Konstanten in Beziehung gesetzt. Es ergaben sich zwei deutlich unterschiedliche Gerade für Verbindungen mit Elektronenakzeptoren und mit Elektronendonatoren als Substituenten, die den *s-trans*- und *s-cis*-quasiplanaren Konformationen zugeordnet wurden. Die mittels der semiempirischen AM1 – Methode berechneten Korrelationen zwischen C=O-Streckfrequenzen und C=O-Bindungsordnungen bzw. Ladungsdichten am Sauerstoffatom ergeben ebenfalls eine Zuordnung der Verbindungen **1** und **2** zu zwei quasiplanaren Konformationen. Die Herstellung einiger neuer Benzoylketen-S,S-acetale wird ebenfalls beschrieben.

Introduction

The concept of push-pull olefinic systems has long been known in chemistry [1, 2]. Substituted benzoylketene-S,S-acetals can be regarded as a typical model for push-pull reaction systems. The ¹H, ¹³C NMR, and M spectra of these compounds have been investigated recently [3, 4]. Now we decided to study the infrared spectra

of a series of substituted benzoylketene-S-S-dimethylacetals (**1a–1o**) and benzoylketene-S,S-ethyleneacetals (**2a–2m**), and to calculate their electronic structure using the semiempirical AM1 method.



1		2	
	X		X
1a	4-OCH ₃	2a	4-OCH ₃
1b	3,4-(CH ₃) ₂	2b	3,4-(CH ₃) ₂
1c	4-CH ₃	2c	4-CH ₃
1d	4-OC ₄ H ₉	2d	4-C ₆ H ₁₁
1e	4-OC ₆ H ₁₃	2e	4-C ₂ H ₅
1f	4-C ₂ H ₅	2f	4-F
1g	4-F	2g	H
1h	H	2h	4-Cl
1i	4-Br	2i	4-Br
1j	3-Br	2j	3-Br
1k	3-CF ₃	2k	4-COCH ₃
1l	4-COCH ₃	2l	3,4-Cl ₂
1m	3,4-Cl ₂	2m	4-NO ₂
1n	2,5-Cl ₂		
1o	4-NO ₂		

Results and Discussion

The characteristic infrared spectral data of compounds **1a–1o** and **2a–2m** are listed in Tables 2 and 3. The carbonyl stretching vibration in all compounds exhibits a single unsplit absorption band in the region of 1635–1617 cm⁻¹ (in CCl₄ and CHCl₃), while the absorption bands corresponding to the C=C stretching vibrations of the vinyl group are observed in the range of 1611–1585 cm⁻¹. Compared to chalcones and other α,β -unsaturated ketones substituted on their benzoyl moiety [9–15], the carbonyl stretching frequencies of substituted benzoylketene-S,S-acetals are markedly shifted to lower values; this effect is caused by enhanced conjugation of the α,β -unsaturated carbonyl system with the lone electron pairs of the two sulfur atoms in the S,S-acetal residue.

Unlike with most α,β -unsaturated ketones [9–15], in benzoylketeneacetals the thermodynamic equilibrium is shifted towards the preference of only one conformation. This is evident from the unsplit feature of the $\nu(\text{C}=\text{O})$ bands and can be accounted for the enforced conjugation between the C=O group and the vinyl moiety.

The carbonyl stretching frequencies of **1a–1o** were correlated with different empirical constants of substituents X. When the original *Hammett* σ constants [16] were used, statistically satisfactory results were obtained. However, the correlation was split into two different well separated and resolved straight lines belonging to

Table 1. Novel substituted benzoylketene-S,S-acetals

	Formula	MW	M.p. (°C) (Solvent)
1b	C ₁₃ H ₁₆ OS ₂	252.40	110–111 (benzene)
1d	C ₁₅ H ₂₀ O ₂ S ₂	296.45	89–90.5 (benzene)
1e	C ₁₇ H ₂₄ O ₂ S ₂	324.51	88–89 (benzene)
1f	C ₁₃ H ₁₆ OS ₂	252.40	52–53 (ether/petroleum ether)
1g	C ₁₁ H ₁₁ FOS ₂	242.34	87.5–89.5 (methanol)
1j	C ₁₁ H ₁₁ BrOS ₂	303.25	78–79 (ethyl acetane)
1k	C ₁₂ H ₁₁ F ₃ OS ₂	292.35	87–88.5 (cyclohexane)
1l	C ₁₃ H ₁₄ O ₂ S ₂	266.38	155–156 (ethanol)
1m	C ₁₁ H ₁₀ Cl ₂ OS ₂	293.24	121–122.5 (benzene)
1n	C ₁₁ H ₁₀ Cl ₂ OS ₂	293.24	162–163 (benzene)
1o	C ₁₁ H ₁₁ NO ₃ S ₂	269.34	171–172 (ethyl acetate)
2b	C ₁₃ H ₁₄ OS ₂	250.39	137–139 (ethanol)
2d	C ₁₇ H ₂₀ OS ₂	304.48	122–124.5 (ethanol)
2e	C ₁₃ H ₁₄ OS ₂	250.39	94–96 (ethanol)
2f	C ₁₁ H ₉ FOS ₂	240.32	108.5–110 (methanol)
2j	C ₁₁ H ₉ BrOS ₂	301.23	90–91.5 (ethanol)
2k	C ₁₃ H ₁₂ O ₂ S ₂	264.37	116–118.5 (ethanol)
2l	C ₁₁ H ₈ Cl ₂ OS ₂	291.22	129.5–131 (ethanol)
2m	C ₁₁ H ₉ NO ₃ S ₂	267.33	236–239 (toluene)

Table 2. Infrared spectral data of benzoylketene-S,S-dimethylacetals **1a–1o**

	$\nu(\text{C=O})(\text{cm}^{-1})$		$\nu(\text{C=C})(\text{cm}^{-1})$	
	CHCl ₃	CCl ₄	CHCl ₃	CCl ₄
1a	1617.5	1628.8	1602.8	1603.2
1b	1618.0	1629.0	1606.5	1607.6
1c	1619.4	1631.0	1606.4	1609.2
1d	1618.0	1628.0	1600.4	1602.4
1e	1618.5	1629.5	1600.4	1602.0
1f	1620.4	1630.4	1606.8	1609.2
1g	1623.2	1633.0	1599.6	1600.0
1h	1628.8	1634.8	1598.8	1599.6
1i	1618.8	1628.9	1588.0	1589.6
1j	1620.4	1630.0	1590.4	1690.0
1k	1621.5	1631.5	1605.2	1607.6
1l	1620.4 ^a	1629.6 ^b	1600.0	1600.0
1m	1621.2	1632.0	1585.2	1587.2
1n	1624.4	1631.6	1596.8	1600.0
1o	1625.6	1633.2	1599.6	1601.2

^a $\nu(\text{C=O})$ for 4-COMe: 1687.2 cm⁻¹; ^b $\nu(\text{C=O})$ for 4-COMe: 1692.8 cm⁻¹

Table 3. Infrared spectral data of benzoylketene-S,S-ethyleneacetals **2a–2m**

	$\nu(\text{C=O})(\text{cm}^{-1})$		$\nu(\text{C=C})(\text{cm}^{-1})$	
	CHCl_3	CCl_4	CHCl_3	CCl_4
2a	1619.5	1627.2	1598.0	1601.6
2b	1620.0	1627.5	1609.0	1609.0
2c	1619.0	1627.2	1609.8	1610.8
2d	1621.0	1627.6	1607.0	1606.4
2e	1621.7	1628.8	1607.5	1608.4
2f	1624.8	1632.0	1597.6	1599.6
2g	1630.5	1633.6	1600.0	1600.0
2h	1620.9	1628.2	1593.2	1592.8
2i	1622.0	1627.8	1590.2	1590.4
2j	1621.0	1631.0	1590.0	1590.0
2k	1622.5 ^a	1629.2 ^b	1598.0	1598.0
2l	1624.6	1630.0	1593.0	1596.8
2m	1629.4	1632.0	1596.8	1600.0

^a $\nu(\text{C=O})$ for 4-COMe: 1688.2 cm^{-1} ; ^b $\nu(\text{C=O})$ for 4-COMe: 1692.8 cm^{-1}

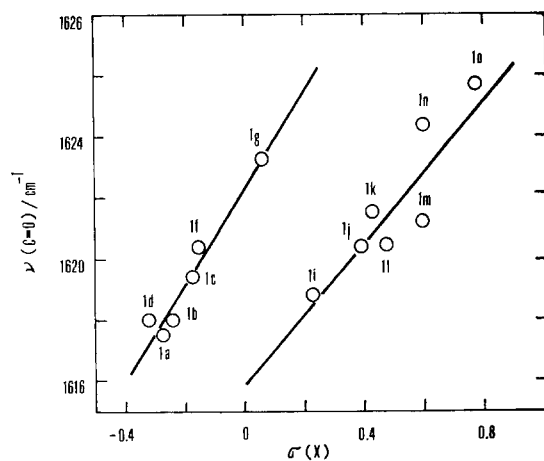


Fig. 1. Dependence of the carbonyl stretching frequencies of substituted benzoylketene-S,S-dimethyl-acetals (CHCl_3) on the Hammett σ values

compounds with electron donor and electron acceptor substituents (see Fig. 1). The straight line corresponding to electron donating substituents can be assigned to a quasiplanar *s-trans* conformation and that corresponding to electron-withdrawing substituents to a quasiplanar *s-cis* conformation:

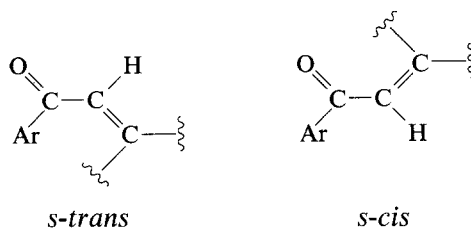


Table 4. Statistical results of $\nu(\text{C}=\text{O})$ vs. σ correlations for substituted benzoylketene-S,S-acetals of series **1** and **2**

Series	Conformation	Solvent	n^a	$\rho \pm s_\rho^b$	z^c	r^d	s^e
1	<i>s-trans</i>	CCl_4	6	13.2 ± 1.5	1632.4	0.975	0.45
1	<i>s-cis</i>	CCl_4	7	7.7 ± 1.7	1627.1	0.896	0.74
1	<i>s-trans</i>	CHCl_3	6	15.5 ± 1.9	1622.2	0.970	0.59
1	<i>s-cis</i>	CHCl_3	7	11.6 ± 2.3	1615.8	0.912	1.01
2	<i>s-trans</i>	CCl_4	6	15.0 ± 2.3	1630.9	0.955	0.62
2	<i>s-cis</i>	CCl_4	6	6.3 ± 2.1	1626.9	0.833	1.00
2	<i>s-trans</i>	CHCl_3	6	15.7 ± 4.1	1623.6	0.886	1.09
2	<i>s-cis</i>	CHCl_3	6	13.5 ± 3.3	1617.3	0.899	1.58

^a number of points used for correlation; ^b slope; ^c intercept; ^d correlation coefficient; ^e standard deviation

An analogous behaviour was also observed with a series of cyclic derivatives, *i.e.* substituted benzoylketene-S,S-ethyleneacetals **2a–2m**. The statistical results of correlations $\nu(\text{C}=\text{O})$ vs. σ (CCl_4 , CHCl_3) for both series of compounds are given in Table 4.

It is known that in the case of substituted isothiocyanatochalcones [17, 18] a similar dependence of the conformational equilibrium exists upon the electronic effects of substituents. The compounds with electron donating substituents exhibit an equilibrium between *s-cis* and *s-trans* conformers, while at substances containing electron withdrawing substituents the *s-cis* conformer is preferred. It is evident from Table 4 that in all cases studied the slopes of the $\nu(\text{C}=\text{O})$ vs. σ correlations are higher for the *s-trans* conformers than for corresponding *s-cis* conformers. This observation is consistent with earlier results obtained for different α,β -unsaturated carbonyl compounds [9–15]. This suggests that the transmission of substituent effects in the more planar *s-trans* conformation is more efficient than in the less planar *s-cis* conformation. Generally, for all substituted benzoylketene-S,S-acetals **1a–1o** and **2a–2m** the slopes of $\nu(\text{C}=\text{O})$ vs. σ correlations are higher than in other α,β -unsaturated carbonyl compounds. This can be explained by the enhanced conjugation supported by resonance interaction between the $\text{CO}-\text{CH}=\text{C}$ moiety and the SCH_3 group.

To confirm the above experimental results, we calculated the electronic structure of the *s-cis* and *s-trans* conformers for a series of substituted benzoylketene-S,S-acetals **1** and **2** using the AM1 method [19] with standard parametrization, whereas with the MMPI method [20] the optimal structures were obtained before. As the infrared spectral data showed the occurrence of both *s-trans* and *s-cis* conformers, the twisting angles between the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups have been determined to be 0° or 180° , respectively. In the optimized structures the electronic structures were studied using the AM1 method. Thereby it was shown that the substituted benzene is twisted out of the plane of the $\text{O}=\text{C}-\text{C}=\text{C}$ group by $83\text{--}87^\circ$ in the case of the *s-trans* isomers, and by only $41\text{--}52^\circ$ in the case of the *s-cis* isomers, which causes a relatively small change in bond orders of the $\text{C}=\text{O}$ group ($p(\text{C}=\text{O})$) and charge

Tables 5. Bond orders $p(\text{C}=\text{O})$ and charge densities $q(\text{O})$ for substituted benzoylketene-S,S-acetals **1a–1o** and **2a–2m**

	$p(\text{C}=\text{O})$	$-q(\text{O})$		$p(\text{C}=\text{O})$	$-q(\text{O})$
1a	1.9224	0.2637	2a	1.9145	0.2714
1b	1.9228	0.2628	2b	1.9145	0.2705
1c	1.9227	0.2627	2c	1.9148	0.2702
1d	1.9227	0.2638	2d	1.9148	0.2704
1e	1.9229	0.2634	2e	1.9151	0.2703
1f	1.9230	0.2624	2f	1.9167	0.2668
1g	1.9245	0.2592	2g	1.8977	0.2728
1h	1.8706	0.2584	2h	1.8990	0.2701
1i	1.9124	0.2547	2i	1.8996	0.2690
1j	1.9141	0.2533	2j	1.9000	0.2692
1k	1.9148	0.2515	2k	1.8983	0.2698
1l	1.9132	0.2545	2l	1.9011	0.2666
1m	1.9156	0.2507	2m	1.8991	0.2573
1n	1.9281	0.2419			
1o	1.9144	0.2420			

Table 6. Statistical results of correlations of $\nu(\text{C}=\text{O})$ values (CHCl_3) with calculated data for benzoylketene-S,S-acetals of series **1** and **2**

Series	Theoretical parameters ^f	Conformation	n^a	ρ^b	z^c	r^d	s^e
1	$p(\text{C}=\text{O})$	<i>s-trans</i>	6	-3627.07	2728.22	0.929	0.81
1	$q(\text{O})$	<i>s-trans</i>	6	1934.23	1199.45	0.952	0.66
1	$p(\text{C}=\text{O})$	<i>s-cis</i>	5	190.77	746.95	0.893	0.54
1	$q(\text{O})$	<i>s-cis</i>	5	1743.28	485.57	0.827	0.68
2	$p(\text{C}=\text{O})$	<i>s-trans</i>	6	-3028.82	2428.01	0.943	0.78
2	$q(\text{O})$	<i>s-trans</i>	6	1938.42	1175.93	0.890	1.07
2	$q(\text{O})$	<i>s-cis</i>	6	1794.02	639.04	0.971	0.87

^{a–e} see footnotes in Table 4; ^f for the missing parameter $p(\text{C}=\text{O})$ for *s-cis* in series **2**, the correlation is statistically of little significance

densities on the oxygen atom ($q(\text{O})$). The data for series **1a–1o** and **2a–2m** are given in Table 5.

Similarly as in the case of $\nu(\text{C}=\text{O})$ vs. σ correlations, the $\nu(\text{C}=\text{O})$ vs. $p(\text{C}=\text{O})$ dependence is clearly split into two straight lines belonging to the *s-cis* and *s-trans* conformers (Fig. 2). The statistical results of linear correlations for C=O bond orders and oxygens atom charge densities with the carbonyl stretching frequencies are listed in Table 6 and are consistent with separation between the compounds with electron donating and electron withdrawing substituents (Table 4 and Fig. 1). The small differences in energies calculated for the *s-cis* and *s-trans* conformers (less than $15 \text{ kJ} \cdot \text{mol}^{-1}$) are probably the reason that the empirical correlations of experimental

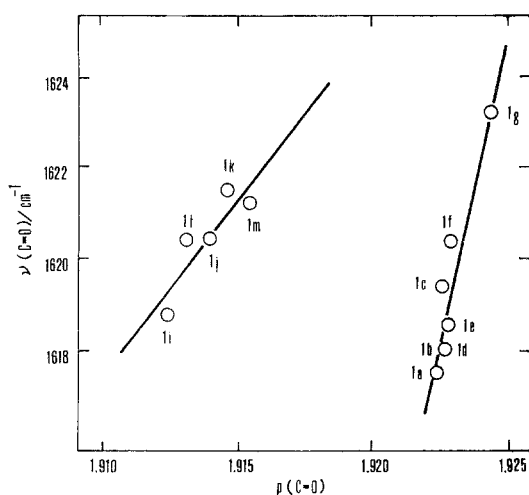


Fig. 2. Dependence of the carbonyl stretching frequencies of substituted benzoylketene-S,S-dimethyl-ketene-S,S-acetals (CHCl_3) on carbonyl bond orders $\rho(\text{C}=\text{O})$

and theoretical parameters are of lower statistical significance. As expected, the calculated values of bond orders for series **2** are somewhat lower compared to those of series **1** which reflects the more electron donating effect of the cyclic $-\text{CH}_2-\text{CH}_2-$ moiety as compared to the CH_3 group [16]. This is, however, in contrast to the sequence of experimental $\nu(\text{C}=\text{O})$ values measured in CHCl_3 and CCl_4 and could be explained as a direct through-space interaction (field effect) between the SCH_3 and $\text{C}=\text{O}$ groups in the case of compounds **1**, which was not included in the semiempirical calculations.

Finally it can be concluded from these results that the substituted benzoylketene-S,S-acetals **1a–1o** and **2a–2m** exist in an equilibrium mixture of *s-trans* and *s-cis* conformers. In the case of electron donating substituents, the *s-trans* conformer is preferred, and for electron withdrawing substituents the *s-cis* conformer is favoured.

Experimental

Compounds **1** and **2** were prepared by dithiocarboxylation of substituted acetophenones with carbon disulfide in the presence of sodium hydride [5] and subsequent alkylation with methyl iodide or 1,2-dibromoethane. Elemental analyses (C, H, N, S) of novel compounds gave satisfactory results.

1-Aryl-3,3-bis-(methylthio)-prop-2-en-1-ones (**1a–1o**)

Sodium hydride (0.01 mol, 2.4 g) was added in portions to a stirred and cooled solution of correspondingly substituted acetophenone (0.05 mol) and carbon disulfide (0.05 mol, 3.8 g) in dry dimethylsulfoxide (150 cm^3). Stirring at room temperature was continued for another 3h, then the mixture was cooled with ice/water and methyl iodide (0.1 mol, 14.2 g) was added dropwise. After stirring 2h at room temperature the mixture was poured into ice/water (250 cm^3). The solid formed was collected by filtration and recrystallized from the solvent indicated in Table 1. Yields: 62–73%.

(1,3-Dithiolan-2-ylidene)-arylmethylketones **2a–2m**

The procedure was the same as described above using 1,2-dibromoethane as alkylation agent. Yields: 52–68%.

Some of the compounds of series **1** and **2** used in this investigation have already been prepared and their analytical and physical data are in agreement with those published [5–8]. The properties of newly prepared compounds of series **1** and **2** are given in Table 1.

The IR spectra of CHCl_3 and CCl_4 solutions in the region of $1700\text{--}1500\text{ cm}^{-1}$ were recorded on a Zeiss M-80 spectrometer at room temperature using NaCl cells of 0.1 and 1.0 mm thickness. The concentration of the measured solutions was chosen to give a maximal absorption of about 70–75%. Solvents purified and dried in a usual manner were used. Peak positions were determined with an accuracy of $\pm 0.1\text{ cm}^{-1}$ against polystyrene standard spectra.

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