INFRARED SPECTRA AND SUBSTITUENT EFFECTS IN 2-(3-, AND 4-SUBSTITUTED PHENYLMETHYLENE)-1,3-CYCLOHEPTANEDIONES

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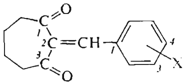
The wave numbers of the fundamental C=O and C=C stretching vibrations, as well as that of the first overtone of C=O stretching vibration of 2-(3-, and 4-substituted phenylmethylene)-1,3-cycloheptanediones and 1,3-cycloheptanedione were measured in tetrachloromethane and chloroform. The spectral data were correlated with σ^+ constants of substituents attached to phenyl group and with wave number shifts of the C=O stretching vibration of substituted acetophenones. The slope of the linear dependence ν *vs* σ^+ of the C=C stretching vibration of the ethylenic group was found to be more than two times higher than that of the analogous correlation of the C=O stretching vibration. Positive values of anharmonicity for asymmetric C=O stretching vibration can be considered as an evidence of the vibrational coupling in a cyclic 1,3-dicarbonyl system similarly, as with derivatives of 1,3-indanedione. The relationship between the wave numbers of the symmetric and asymmetric C=O stretching vibrations indicates that the effect of structure upon both vibrations is symmetric. The vibrational coupling in 1,3-cycloheptanediones and the application of Seth-Paul-Van Duyse equation is discussed in relation to analogous results obtained for other cyclic 1,3-dicarbonyl compounds.

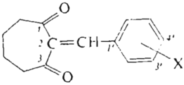
Our preceding papers[1-8] dealt with the C=O stretching vibrations of some cyclic 1,3-diketones and showed the electronic effects of substituents upon these vibrations. The linear relations between the wave numbers of symmetric and asymmetric C=O stretching vibrations were employed by investigating the vibrational coupling and geometry in a cyclic 1,3-dicarbonyl system[1,5-7]. The most recent results showed[9,10] that investigation of the first overtones and the mechanical anharmonicity might be of use when clearing and proving the vibrational coupling causing a splitting of the

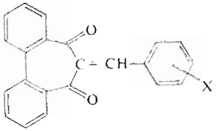


Ia, X = 4-N$(CH_3)_2$ *Ib*, X = 4-OH *Ic*, X = 4-OCH_3
Id, X = 4-CH_3 *Ie*, X = 4-F *If*, X = H
Ig, X = 4-Cl *Ih*, X = 4-Br *Ii*, X = 4-CN
Ij X = C-NO_2 *Ik*, X = 4-NO_2

absorption band of the C=O stretching vibration in cyclic 1,3-dicarbonyl compounds.

This paper is aimed to study the relationships between the spectral data and structure of 1,3-cycloheptanediones in relation to other cyclic 1,3-dicarbonyl systems. Therefore, wave numbers of fundamental C=O and C=C stretching vibrations and those of the first overtone of the C=O stretching vibrations of 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones *I* and 1,3-cycloheptanedione were measured and compared with spectral data of dibenzo analogues of 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones[7] *II*.





II

EXPERIMENTAL

Compounds of general formula *I* were synthesized according to[11]. The synthesis of cycloheptanedione, the properties and detailed preparation of *I* are being reported elsewhere[12].

The infrared spectra of CCl_4 and $CHCl_3$ solutions of compounds were taken on a Zeiss, model 75 IR Specord, and Perkin-Elmer, model 567 grating spectrophotometers using cells of 0·1, 1, 5 and 60 mm thickness. Concentration of the measured solutions met requirement for a 70—75% maximum of the bands examined. The absorption band peaks were read with a ±0·5 cm^{-1} accuracy. The wave numer scale was calibrated against reference spectra of both indene and atmospheric water vapour.

Data for σ^+ constants of substituents, reported in[13] and well-characterized σ values collected in[14] were employed for linear correlations of wave numbers. The wave number shifts of the C=O stretching vibration $\Delta\nu_{AF}$ of substituted acetophenones were calculated according to equation

$$\Delta\nu_{AF} = \nu(C{=}O)_{XC_6H_4COCH_3} - \nu(C{=}O)_{C_6H_5COCH_3}$$

using values in CCl_4 as reported by Laurence and Berthelot[15].

RESULTS AND DISCUSSION

Wave numbers of the fundamental C=O and C=C stretching vibrations and those of the first overtone of the C=O stretching vibrations of 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones *I* measured in dilute CCl_4 or $CHCl_3$ solutions are listed in Tables I and II. Following values of wave numbers of C=O stretching vibration (in cm^{-1}) were measured for 1,3-cycloheptanedione: $\nu_{01(s)} = 1\,730{\cdot}5$, $\nu_{01(as)} = 1\,706$, $\nu_{02(s)} = 3\,443$, $\nu_{02(as)} = 3\,412$ in CCl_4; $\nu_{01(s)} = 1\,723{\cdot}5$, $\nu_{01(as)} = 1\,700{\cdot}5$ in $CHCl_3$.

TABLE I

Wave numbers (cm^{-1}) both of the fundamental C=O stretching vibration and the first overtone in CCl_4 for the series of 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones *I*

Compound	$\nu_{01(s)}$	$\nu_{01(as)}$	$\tilde{\nu}_{01}$	$\nu_{02(s)}$	$\nu_{02(as)}$	$\tilde{\nu}_{02}$
Ia	1 688·0	1 658·5	1 673·2	[a]	[a]	—
Ib	1 704 0	1 681·5	1 692·7	[b]	3 370 0	—
Ic	1 704·5	1 682·0	1 693·2	3 401·5	3 370 0	3 385·7
Id	1 706·0	1 684·0	1 695·0	3 405·5	3 374·0	3 389·7
Ie	1 708·0	1 684·5	1 696·2	3 406·5	3 376·5	3 391·5
If	1 707·0	1 687·0	1 697·0	3 407·0	3 374·5	3 390·7
Ig	1 708·5	1 686·0	1 697·2	3 411·0	3 378·5	3 394·7
Ih	1 708·0	1 687·0	1 697·5	3 411·5	3 379·0	3 395·2
Ii	1 711·0	1 688·5	1 699·7	3 410·5	3 383·5	3 397·0
Ij	1 711·0	1 688·5	1 699·7	3 412·5	3 384·0	3 398·2
Ik	1 711·5	1 688·5	1 700·0	3 414·0	3 384·0	3 399·0

[a] Low solubility; [b] low solubility and overlapping with ν(OH).

TABLE II

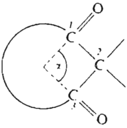
Wave numbers (cm^{-1}) of the C=O and C=C stretching vibrations in $CHCl_3$ for the series of 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones *I*

Compound	C=O			C=C
	$\nu_{01(s)}$	$\nu_{01(as)}$	$\tilde{\nu}_{01}$	ν_{01}
Ia	1 679·0	1 648·0	1 663·5	1 570·0
Ib	1 693·5	1 674·0	1 683·7	1 576·0
Ic	1 698·0	1 674·5	1 686·2	1 587·0
Id	1 701·0	1 678·0	1 689·5	1 593·0
Ie	1 703·5	1 679·5	1 691·5	1 600·0
If	1 703·0	1 680 5	1 691·7	1 597·0
Ig	1 704·5	1 681·0	1 692·7	1 597·0
Ih	1 704·0	1 682·5	1 693·2	1 599·0
Ii	1 706·5	1 684·5	1 695·5	1 604·5
Ij	1 707·0	1 684·0	1 695·0	1 606·0
Ik	1 707·0	1 684·0	1 695·5	1 611·5

Similarly as other cyclic 1,3-dicarbonyl compounds existing in a diketo form, compounds *I* also reveal two absorption bands in the wave number region of fundamental C=O stretching vibrations; the lower wave number, more intese band belongs to the asymmetric ($\nu_{01(as)}$) vibration, and the weaker one at the higher wave number to the symmetric ($\nu_{01(s)}$) vibration of the coupled 1,3-dicarbonyl system. The absorption bands ν_s and ν_{as} of the 1,3-cycloheptanedione and its derivatives *I* appeared at higher wave numbers when compared with dibenzo derivatives *II*, this being caused by an isolation of carbonyl group in a saturated seven-membered ring.

As known, the difference between the wave number of the symmetric and asymmetric stretching C=O vibration $\Delta\nu = \nu_s - \nu_{as}$ can be considered a measure of the vibrational coupling in a 1,3-dicarbonyl system. As observed by Fayat and Foucaud[17], the $\Delta\nu$ values depend in the first approach on the magnitude of the angle α, formed by two vibrating C=O bands in a cyclic system. The magnitude of this angle is a function of both the structure and geometry of the ring on one hand, and the electronic structure of $C_{(2)}$ and its close exocyclic environment on the other.

The $\Delta\nu$ values for compounds *I* appear within $20-30\ \text{cm}^1$ and are, on average by $10\ \text{cm}^{-1}$ lower than those for dibenzo derivatives *II* (ref.[7]), and by $15-20\ \text{cm}^{-1}$ lower than for five-membered cyclic 1,3-diketones[1,6,16]. A successive lowering of the vibrational coupling degree from a five-membered system through dibenzo derivatives *II* to compounds *I* can be interpreted in the first approach as an enlargement of the ring and extension of the C=C bond length in the ring resulting in diminution of the angle α.



SCHEME 1

Derivatives of 1,3-cycloheptadione *II* revealed in the $3\,450-3\,370\ \text{cm}^{-1}$ region couple of absorption bands ascribable to the first overtone of the symmetric $\nu_{02(s)}$ and asymmetric $\nu_{02(as)}$ C=O stretching vibration. The mechanical anharmonicities of vibration $\omega_e x_e$ can be calculated from the equation

$$\omega_e x_e = (\nu_{02} - 2\nu_{01})/2$$

employing the wave numbers of the first overtones and the double of wave numbers of the corresponding fundamental vibrations.

The symmetric C=O stretching vibration for 1,3-cycloheptanediones gives negative values of $\omega_e x_e = -2$ to $-19\ \text{cm}^{-1}$, this being analogous to vibrations of many common carbonyl compounds having a weak, or none vibrational interaction[18-20]. On the other hand, the mechanical anharmonicity values for the asymmetric C=O stretching vibration are either positive or close to zero $\omega_e x_e = 0$ to $+4\ \text{cm}^{-1}$. This phenomenon has been found with derivatives of 1,3-indanedione and other cyclic 1,3-dicarbonyl compounds, having not only the rigid *W*, but also *U* conformation[9,10] as well. The anharmonicities for ν_{as} are even more pronounced towards positive values in more coupled systems[16]. As follows, the anharmonicity of the asymmetric stretching vibration can serve for evidencing, or alternatively for a quantitative evaluation of the vibrational coupling in a cyclic 1,3-dicarbonyl system.

Absorption bands of C=C stretching vibration of the $>$C=CH— group of *I* appear at 1 612–1 570 cm^{-1} in $CHCl_3$; they can be distinguished from those of the benzene ring by a higher absorption intensity, and, by comparison with spectra of compounds without aromatic systems[21-24]. Differences between the arithmetic means of ν_s(C=O) and ν_{as}(C=O) values and the wave numbers of C=C stretching vibration are in accordance with analogous values of compounds[23,24], having the C=O bond in an *s-cis* conformation with respect to the C=C bond.

Correlation Analysis

The arithmetic means of wave numbers of the fundamental symmetric and asymmetric C=O stretching vibration ($\tilde{\nu}_{01}$) of compounds *I* in CCl_4 and $CHCl_3$ correlate with the Brown–Okamoto σ^+ constants of substituents X. The employment of the Hammett values afforded statistically less significant results. The suitability of the

TABLE III

Linear correlations $y = \varrho x + q$ for spectral data of 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones *I*

y	x	Solvent	n^a	r^b	ϱ	q	s^c
$\tilde{\nu}_{01}$(C=O)	σ^+	CCl_4	10	0·998	4·44 ± 0·11	1 696·7	0·2
$\tilde{\nu}_{01}$(C=O)	$\Delta\nu_{AF}$	CCl_4	10	0·989	0·365 ± 0·02	1 696·6	0·4
$\tilde{\nu}_{01}$(C=O)	σ^+	$CHCl_3$	10	0·981	6·73 ± 0·46	1 691·3	0·8
$\tilde{\nu}_{02}$(C=O)	σ^+	CCl_4	9	0.973	8·42 ± 0·75	3 392·4	1·1
ν_{01}(C=C)	σ^+	$CHCl_3$	10	0·984	15·08 ± 0·96	1 597·2	2·2
$\nu_{01(s)}$	$\nu_{01(as)}$	CCl_4, $CHCl_3$	21^d	0·990	1·02 ± 0·03	−8·2	1·0

[a] Number of experimental points employed for correlation; [b] correlation coefficient; [c] standard deviation; [d] values $\nu_{01(s)}$ and $\nu_{01(as)}$ in CCl_4 and $CHCl_3$ for 1,3-cycloheptanedione were taken into correlation.

arithmetic means of wave numbers of symmetric and asymmetric vibrations, as well as the σ^+ constants for cyclic 1,3-diketones have already been discussed[2-5,7]. The statistical results of linear dependences for the spectral data of 1,3-cycloheptanediones are listed in Table III. The $\bar{\nu}_{01}(C{=}O)$ values for compounds *I* have a satisfying linear correlation also wih wave number shifts of the C=O stretching vibrations of acetophenones ($\Delta\nu_{AF}$). Similar correlations were recently[15] used to evaluate the transmission of electronic effects in various series of carbonyl compounds. Relationships of the $\nu(C{=}O)$ *vs* $\Delta\nu_{AF}$, (or ν_{AF}) type were recently reported[9,10] also for some 1,3-dicarbonyl systems.

The slopes of linear correlation $\bar{\nu}_{01}(C{=}O)$ *vs* σ^+ for a series of compounds *I* in CCl_4 and in $CHCl_3$ are by approximately 13% lower than those of dibenzo derivatives *II*. The higher sensitivity of carbonyl groups towards electronic effects in compounds *II* is due to the enhancement of their electron-accepting effect resulting from the conjugation with π-electrons of two benzene rings. A similar sensitivity increase of carbonyl compounds towards substituent effects was encountered with five-membered rings transition from 2-(arylmethylene)-1,3-indanediones[2] to 2-(arylmethylene)-1,3-benz[*f*]indanediones[5]; this behaviour can be explained analogously as with the preceding case.

The arithmetic means of the first overtone wave numbers of the symmetric and asymmetric C=O stretching vibration ($\bar{\nu}_{02}$) of cycloheptanedione derivatives *I*, which are very close to the twice of arithmetic means of the corresponding fundamental vibrations, also afford a statistically significant correlation with σ^+ constants of substituents. This fact is in line with a theoretical presumption[25] that the characteristics of vibration can be transferred also in the anharmonic approximation. More-

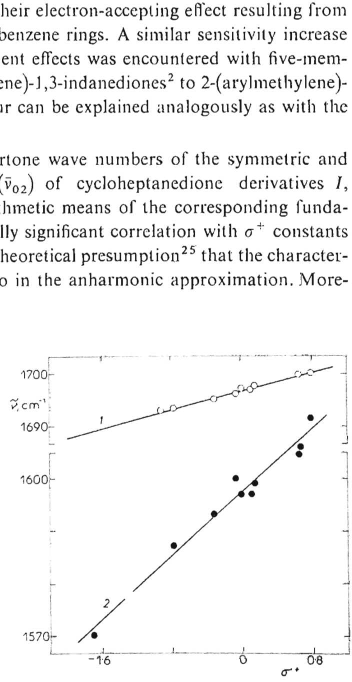
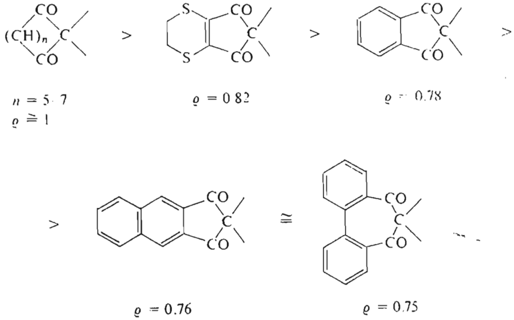


FIG. 1

Relationship between the arithmetic means of wave numbers of symmetric and asymmetric fundamental C=O and wave numbers C=C stretching vibrations and σ^+ constants of substituents for 2-(3-, and 4-X-phenylmethylene)-1,3-cycloheptanediones *I*. 1 $\tilde{\nu}_{01}$.(C=O) *vs* σ^+, 2 ν_{01}(C=C) *vs* σ^+

over, the slope of $\bar{\nu}_{02}(C{=}O)$ *vs* σ^+ corresponds approximately to the double of the slope of correlation $\bar{\nu}_{01}(C{=}O)$ *vs* σ^+ associated with the fact that transitions expressed by $\bar{\nu}_{02}(C{=}O)$ are *quasi* harmonic.

The wave number of the C=C stretching vibration of the exocyclic $\gt C{=}CH{-}$ grouping of compounds of series *I* affords a good linear relationship on σ^+ constants of substituents. Table III documents the value of the slope of relationship to be by more than two times higher than that of an analogous relationship for wave numbers of C=O stretching vibration (*cf.* Fig. 1). This effect can be also observed with other systems[26], having the C=O group in an *s-cis* conformation in respect to the C=C bond. Thus, *e.g.* for α,β-unsaturated aromatic ketones[23] and substituted 3-(phenylmethylene)-2,4-pentanediones[10] the slope ratio $\varrho(C{=}O)/\varrho(C{=}C)$ of the linear relationship $\nu(C{=}O)$ *vs* σ^+ for *s-cis* conformation makes about 0·5.



SCHEME 2

Like in the series of other cyclic 1,3-diketones[1,5–7], 1,3-cycloheptanedione reveals a linear correlation between the wave number of symmetric and asymmetric C=O stretching vibration; data obtained in CCl_4 and in $CHCl_3$ lie on the same line (Fig. 2). The slope of this dependence is close to one, and consequently, the ν_s is approximately equally sensitive towards electronic effects as ν_{as}. A similar slope of correlations ν_s *vs* ν_{as} was reported[17] for wave number of the C=O stretching vibration of 1,3-cyclohexanediones and 1,3-cyclopentanediones. On the other hand, other cyclic 1,3-diketones as 1,3-indanediones[1] 1,3-benz[*f*]indanediones[5], 5,6-dihydro-4,7-dithia-1,3-indanediones[6] and dibenzo analogues of 1,3-cycloheptanediones exhibit the slope of ν_s *vs* ν_{as} correlation always lower than 1. This nonsymmetrical effect of structure upon ν_s and ν_{as} of the afore-mentioned examples is due a direct conjugation between two C=O groups having the vibrations mechanically coupled. Compound *I*, similarly as other saturated cyclic 1,3-diketones[17] are lacking this conjugation and therefore, the electronic effects of the close environment of C=O groups shall affect symmetrically both types of vibrations ν_s and ν_{as}. In systems containing conjugated multiple bonds in the ring, the asymmetry of the electronic effects upon ν_s and ν_{as} shall depend on the degree of mesomeric interaction between the two carbonyl groups. According to this concept, the decreasing slopes of dependences ν_s *vs* ν_{as} for hitherto investigated systems can be arranged in a series of increasing mesomeric interaction between C=O groups.

Arithmetic means of wave numbers of the symmetric and asymmetric fundamental C=O stretching vibrations in CCl_4 for 42 derivatives of 1,3-cycloheptanedione I and dibenzo analogues *II* (ref.[7]) can be correlated with $X^+(R)$ constants of structural fragments in the sense of improved and extended Seth-Paul-Van Duyse equation[27]

$$\bar{\nu}_{01}(C=O) = 33{\cdot}45\,(\pm 0{\cdot}84) \sum X^+(R) + 1\,565{\cdot}2 \qquad (1)$$

$$r = 0{\cdot}988\,, \quad s = 2{\cdot}2$$

Dismembering the 1,3-cycloheptanedione structure into structural fragments, as well as the method of calculation of the additive $X^+(R)$ constants of the structural fragments is described[28] in more detail.

The equation (*1*) upon comparison with an analogous relationship for 1,3-indanediones[8]

$$\bar{\nu}_{01}(C=O) = 33{\cdot}09\,(\pm 0{\cdot}70) \sum X^+(R) + 1\,610{\cdot}6 \qquad (2)$$

$$r = 0{\cdot}991\,, \quad s = 2{\cdot}0$$

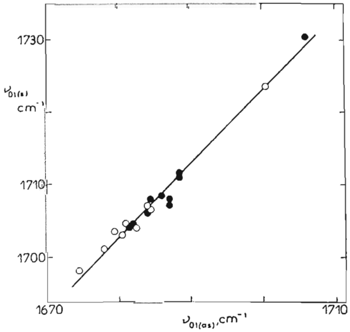


FIG. 2

Relationship between the wave number of symmetric and asymmetric C=O stretching vibration for 1,3-cycloheptanedione derivatives. ● in CCl_4, ○ in $CHCl_3$

shows that the slopes of both correlations are virtually identical, and the lines are shifted parallel along the wave number axis by approximately 46 cm^{-1}. As it follows, introduction of $X^+(R)$ constants in the sense of Seth-Paul-Van Duyse equation makes the sensitivity of two various cyclic 1,3-dicarbonyl systems unified towards effects of the structural environment, notwithstanding whether the C=O groups are in a five- or a seven-membered ring. Difference between the intercepts on the wave number axis for linea (1) and (2) is associated with the enhancement of wave numbers of vibrations of the C=O group when contracting the ring size from seven- to a five-membered ring. As already reported[29] a similar phenomenon was encountered also with cyclic monocarbonyl compounds; this was rationalized by the change of an sp^2 hybridization of the C atom of the carbonyl group due to diminuation of valence angles in the ring. This effect is not, however, included in the calculation of $X^+(R)$ constants of 1,3-dicarbonyl structural fragments. Even though the application of Seth-Paul-Van Duyse equation on specific structure of cyclic 1,3-diketones has some restrictions, the general trend of results is as follows: the arithmetic means of wave number $\nu_{(s)}$ and $\nu_{(as)}$ of five- and seven-membered cyclic 2,3-diketones correlate with $X^+(R)$ constants of structural fragments according to equation

$$\bar{\nu}_{01}C{=}O) = 33 \sum X^+(R) + B\,, \tag{3}$$

where B is the constant for the proper ring partly dependent on the ring size.

It could be, therefore, concluded that the Seth-Paul-Van Duyse equation is satisfactorily applicable even for wave numbers of the C=O stretching vibration of 1,3-cycloheptanediones. Results of our preceding papers[8,27,28,30,31], those of the presented paper and also those of other authors[32] provided evidence that the improved Seth-Paul-Van Duyse equation can be applied for about 1 000 carbonyl and dicarbonyl compounds.

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