Monatshefte für Chemie 130, 515–523 (1999)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Structure-Reactivity-Spectra Correlations for Substituted 3,4-Diphenylcyclobut-3-ene-1,2-diones

Alexander Perjéssy[1,*], **Keith Bowden**[2], **Walter M. F. Fabian**[3],
Ol'ga Hritzová[4], **Nad'a Prónayová**[5], **Zora Šusteková**[1],
and **Abdulaziz Al-Najjar**[2]

[1] Department of Organic Chemistry and Institute of Chemistry, Faculty of Natural Sciences, Comenius University, SK-84215 Bratislava, Slovak Republic
[2] Department of Biological and Chemical Sciences, University of Essex, Colchester CO4 3SQ, United Kingdom
[3] Institute of Organic Chemistry, Karl Franzens University, A-8010 Graz, Austria
[4] Department of Organic Chemistry, Faculty of Natural Sciences, P. J. Šafárik University, SK-04167 Košice, Slovak Republic
[5] Central Laboratories, Faculty of Chemical Technology, Slovak Technical University, SK-81237 Bratislava, Slovak Republic

Summary. The infrared absorption bands of the C=O stretching vibration and the ^{13}C NMR chemical shifts were measured for a series of nine substituted 3,4-diphenyl-cyclobut-3-ene-1,2-diones in $CHCl_3$, $CDCl_3$, and partially in CCl_4. The AM1 charge densities, bond orders, and valence angles were calculated for the optimized geometry. Good to satisfactory mutual correlations were found between the arithmetic means of the wave numbers of symmetric and asymmetric C=O stretching vibrations, *Hammett* σ constants, rate coefficients, and enthalpies of activation of the base-catalyzed ring fission as well as the AM1 oxygen charge densities and bond orders at the carbonyl groups. The results show that the factors controlling the reactivity of these compounds and the structural and IR spectroscopic properties of the C=O groups must be the same. The correlation between the wave numbers of symmetric and asymmetric C=O stretching vibrations affords a slope of $a = 1.069$ which points to the existence of a strong cross-conjugation effect in the cyclobutenedione ring. The correlation of the wave number separation of the absorption bands of symmetric and asymmetric C=O stretching vibrations ($\Delta\nu$(C=O)) for various cyclic diketones enabled the prediction of the angle $\gamma = 83°$ between the bond vectors of the two carbonyl groups in the cyclobutenedione rings, which is in satisfactory agreement with the value calculated by the semiempirical AM1 method.

Keywords. 3,4-Diphenylcyclobut-3-ene-1,2-diones; ^{13}C NMR; IR; AM1 calculations; Correlation analysis.

---

[*] Corresponding author

Korrelationen zwischen Struktur, Reaktivität und Spektren für substituierte 3,4-Diphenylcyclobut-3-en-1,2-dione

Zusammenfassung. Die Infrarotabsorptionsbanden der C=O Streckschwingung und die chemischen Verschiebungen der ^{13}C NMR Signale wurden für eine Reihe von neun substituierten 3,4-Diphenylcyclobut-3-en-1,2-dionen in $CHCl_3$, $CDCl_3$ und teilweise in CCl_4 gemessen. Die AM1-Ladungsdichten, Bindungsordnungen und Bindungswinkel wurden für die Optimalgeometrie berechnet. Zwischen den arithmetischen Mitteln der symmetrischen und asymmetrischen C=O-Streckschwingung, den *Hammett*schen σ-Konstanten, den Geschwindigkeitskoeffizienten und Aktivierungsenthalpien der basenkatalysierten Ringspaltung sowie den AM1-Sauerstoffladungsdichten und Bindungsordnungen der Carbonylgruppen wurden gute bis befriedigende Korrelationen gefunden. Die Resultate zeigen, daß die Faktoren, die die Reaktivität dieser Verbindungen kontrollieren, dieselben sind wie jene, die die strukturellen und IR-spektroskopischen Eigenschaften bedingen. Die Korrelation zwischen den Wellenzahlen der symmetrischen und der asymmetrischen C=O-Streckschwingung hat einen Anstieg von $a = 1.069$, was auf einen starken Kreuzkonjugationseffekt im Cyclobutendionring hinweist. Die Korrelation der Wellenzahlenseparation der symmetrischen und asymmetrischen C=O Streckschwingungen ($\Delta\nu$(C=O)) für verschiedene zyklische Diketone läßt einen Winkel von $\gamma = 83°$ zwischen den Bindungsvektoren der beiden Carbonylgruppen des Cyclobutendionringes erwarten, der ausgezeichnet mit dem durch die semiempirische AM1-Rechnung erhaltenen übereinstimmt.

Introduction

3,4-Diphenylcyclobut-3-ene-1,2-dione (**5**) represents a stable and structurally interesting small cyclic molecule which could serve as an intermediate for the realization of *bona fide* cyclobutadienes [1] used also in the synthesis of natural pheromones [2]. The solid-state infrared spectra of **5** have been studied in KBr [1]. The region of the carbonyl stretching vibrations has been described as a doublet at 1786 and 1776 cm^{-1}, accompanied by a shoulder at 1761 cm^{-1}. This doublet is generally assigned to the symmetric and asymmetric stretching vibrational modes of the two carbonyl groups in a coupled cyclic 1,2-dicarbonyl system [3, 4]. The assignment of the ^{13}C NMR signals of **5** has also been reported [6]. However, the ^{13}C NMR data for the substituted compounds **1**–**4** and **6**–**9** have not been published previously.

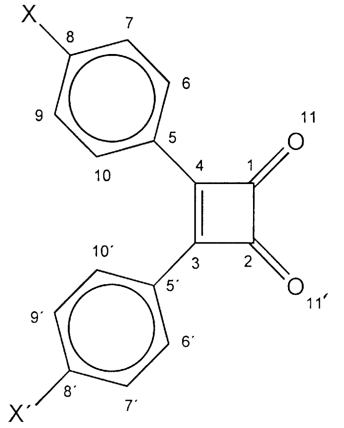
Recently, the mechanism of the base catalyzed ring fission of the substituted 3,4-diphenylcyclobut-3-ene-1,2-diones **1**–**9** has been investigated, and the rate coefficients have successfully been correlated using the *Hammett* equation [5]. Our recent studies have shown that the correlation of the kinetic behaviour of the base-catalyzed ring fission of derivatives and analogues of isobenzofuranones with IR, NMR, and theoretical characteristics of the C=O group involved in the reaction can serve as an effective way for a better understanding and explanation of the reaction mechanism and the structures of the reactants [7–10].

The aim of the present investigation is to study the IR and ^{13}C NMR spectra and to calculate theoretical parameters for a series of substituted 3,4-diphenylcyclobut-3-ene-1,2-diones (**1**–**9**, Scheme 1) and to compare the results with previously published kinetic data [5].

Results and Discussion

The ^{13}C NMR chemical shifts and their assignments for compounds **1**–**9** are given in Table 1. The assignments for the parent compound **5** are identical with those reported [6]. The chemical shifts of C(1)–C(4) were assigned using HETCOR and a semiselective INEPT (SINEPT) experiments [11]. It is evident that the substituent effect on the ^{13}C NMR signals of the carbonyl groups is very small, the maximal change of $\delta(C^{(1)})$ and $\delta(C^{(2)})$ being only 1.4 ppm. On the other hand, the chemical shifts of the carbon atoms of the cyclobutenedione ring ($\delta(C^{(3)})$ and $\delta(C^{(4)})$ show greater variation; however, they, do not show any regular alternation or linear correlation with the electronic properties of the substituents X and X' attached to the benzene rings (Scheme 1). However, the disubstituted systems (compounds **1**, **3**, **5**, **8**, **9**) do show the spectral symmetry expected.

The AM1 results, *i.e. Coulson* and *Mulliken* oxygen atom charge densities as well as the carbonyl group bond orders and, finally, the angles between the bond vectors of the two C=O groups for compounds **1**–**9** are listed in Table 2.



	X	X'
1	OCH_3	OCH_3
2	H	OCH_3
3	CH_3	CH_3
4	H	CH_3
5	H	H
6	H	Cl
7	H	Br
8	Cl	Cl
9	Br	Br

Scheme 1

Table 1. ^{13}C NMR chemical shifts (δ, ppm) for compounds **1**–**9**; for numbering of carbon atoms, see Scheme 1

	1	2	3	4	5	5′	6	6′	7	7′	8	8′	9	9′	10	10′
1	196.3	196.3	184.4	184.4	121.2	121.2	130.4	130.4	114.7	114.7	163.5	163.5	114.7	114.7	130.4	130.4
2	196.8	195.7	186.4	185.3	120.9	128.5	130.8	127.9	114.8	129.2	164.0	132.8	114.8	129.2	130.8	127.9
3	196.4	196.4	186.5	186.5	125.6	125.6	128.3	128.3	130.0	130.0	144.5	144.5	130.8	130.0	128.3	128.3
4	196.5	196.1	187.4	186.5	125.5	128.2	128.1	128.2	130.1	129.3	144.8	133.1	130.1	129.3	128.1	128.2
5	196.2	196.2	187.5	187.5	128.1	128.1	128.2	128.2	129.3	129.3	133.4	133.4	129.3	129.3	128.2	128.2
6	195.7	195.7	187.6	185.8	126.5	127.9	129.8	128.2	129.5	129.5	139.7	133.6	129.5	129.5	129.8	128.2
7	195.7	195.7	188.3	186.0	126.9	128.0	129.5	128.2	132.8	129.5	128.0	133.6	132.8	129.5	129.5	128.2
8	195.4	195.4	185.9	185.9	126.3	126.3	129.9	129.9	129.5	129.5	140.0	140.0	129.5	129.5	129.9	129.9
9	195.3	195.3	186.1	186.1	126.7	126.7	129.5	129.5	133.0	133.0	128.6	128.6	133.0	133.0	129.5	129.5

Table 2. AM1 theoretical results for compounds **1–9**

	$q(O^{(11)})$[a]	$q(O^{(11')})$[a]	$q(O^{(11)})$[b]	$q(O^{(11')})$[b]	$P(C^{(1)}O^{(11)})$	$P(C^{(2)}O^{(11')})$	γ(°)[c]
1	−0.2251	−0.2251	−0.2597	−0.2597	1.9460	1.9460	93.2
2	−0.2214	−0.2208	−0.2568	−0.2554	1.9492	1.9510	93.2
3	−0.2211	−0.2211	−0.2556	−0.2556	1.9503	1.9503	93.2
4	−0.2202	−0.2199	−0.2548	−0.2545	1.9509	1.9517	93.3
5	−0.2191	−0.2191	−0.2537	−0.2536	1.9524	1.9524	93.2
6	−0.2156	−0.2179	−0.2502	−0.2524	1.9556	1.9534	93.4
7	−0.2145	−0.2169	−0.2491	−0.2514	1.9569	1.9542	93.4
8	−0.2145	−0.2145	−0.2490	−0.2491	1.9566	1.9566	93.5
9	−0.2124	−0.2124	−0.2469	−0.2470	1.9587	1.9587	93.6

[a] *Coulson* charge density; [b] *Mulliken* charge density; [c] see Scheme 2

Table 3. IR spectroscopic results (cm^{-1}) for compounds **1–9** in CHCl$_3$[a]

	ν_s(C=O)	ν_{as}(C=O)	ν_{comb}	$\Delta\nu$(C=O)[b]
1	1780.5 (2.17)	1767.1 (0.89)	1756.4 (1.52)	13.4
	1782.4[c]	1776.3[c]	1747.1[c]	6.1[c]
2	1780.8 (2.00)	1767.2 (0.64)	1755.1 (1.28)	13.6
3	1778.0 (1.65)	1767.0 (0.32)	1754.7 (1.78)	13.0
4	1782.4 (1.76)	1769.5 (0.91)	1755.9 (0.86)	12.9
5	1783.0 (2.00)	1770.6 (1.25)	1750.0 (0.43)	13.0
	1783.2[c]	1776.9[c]	1750.2[c]	6.3[c]
6	1783.0 (2.23)	1770.3 (0.86)	1756.8 (0.74)	12.4
7	1783.4 (2.23)	1770.3 (0.98)	1754.0 (0.36)	13.1
8	1784.5 (1.85)	1771.9 (0.93)	1757.7 (0.32)	12.6
	1782.4[c]	1776.0[c]	1748.1[c]	6.4[c]
9	1785.6 (1.51)	1772.2 (0.74)	1751.9 (0.21)	13.4

[a] After band separation, integrated intensities (l · mol^{-1} · cm^{-2}) are given in parentheses; [b] wave number separation of the symmetric and asymmetric stretching vibrations: $\Delta\nu(C=O) = \nu_s(C=O) - \nu_{as}(C=O)$; [c] measured in CCl$_4$

The infrared spectroscopic characteristics of the cyclobutenedione ring for **1**–**9** are shown in Table 3. The wave numbers of the band maxima and the integrated intensities were obtained after deconvolution and separation of the three overlapping absorption bands measured in CHCl$_3$ in the region of 1790–1750 cm^{-1}. The most intensive absorption band (1785.6–1780.5 cm^{-1}) was assigned to the symmetric stretching vibrational mode of the mechanically coupled cyclic 1,2-dicarbonyl system, whereas the closer and less intensive branch of the doublet (1772.2–1767.0 cm^{-1}) belongs to the asymmetric C=O stretching vibration. The wave numbers separation of the absorption bands of the symmetric and asymmetric stretching vibrations ($\Delta\nu$(C=O)) is almost constant and occurs in a very narrow range (12.4–13.4 cm^{-1}). The ratio of the integrated intensities of the bands of asymmetric and symmetric C=O stretching vibrations varies between 0.2 and 0.6. The wave numbers of both above-mentioned absorption bands in CHCl$_3$

Table 4. Kinetic data[a] and substituent constants[b] for compounds **1–9**

	$\log k_2$ (25°C)	$\log k_2$ (45°C)	$\Delta H^{\ddagger}$	$\Sigma\sigma$
1	1.041	1.350	6.10	−0.54
2	1.342	1.608	5.20	−0.27
3	1.393	1.680	5.60	−0.34
4	1.608	1.869	5.10	−0.17
5	1.849	2.068	4.15	0.00
6	2.090	2.279	3.50	0.23
7	2.107	2.324	4.10	0.23
8	2.326	2.530	3.80	0.46
9	2.371	2.572	3.75	0.46

[a] k_2 in $\mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$, $\Delta H^{\ddagger}$ in $\mathrm{kcal \cdot mol^{-1}}$, in 50% (v/v) aqueous *DMSO*, taken from Ref. [5]; [b] $\Sigma\sigma = \sigma_p(X) + \sigma_p(X')$, σ_p taken from Ref. [12]

exhibit a regular increase as the electron-donating properties of substituents *X* and *X′* change to electron-withdrawing ones. The third (lowest) absorption band (1757.7–1751.9 $\mathrm{cm^{-1}}$) is, in most cases, the least intensive one, and its relation to the electronic properties of substituents is completely irregular. Therefore, this absorption band may probably be assigned to a combination vibration of two (deformation?) vibrations at ~900 and ~800 $\mathrm{cm^{-1}}$.

In Table 4, the kinetic data for the base-catalyzed ring fission of compounds **1**–**9** (*i.e.* the rate coefficients (k_2) and the enthalpies of activation ($\Delta H^{\ddagger}$)) which have been discussed recently [5] are shown together with the values of the *Hammett* substituent constants which are employed in the correlation analysis of the results.

Similar to the case of cyclic 1,3-diketones [13–16], the arithmetic mean of the wave numbers of symmetric and asymmetric C=O stretching vibrations for compounds **1**–**9**, $\bar{\nu}(\mathrm{C{=}O}) = (\nu_s(\mathrm{C{=}O}) + \nu_{as}(\mathrm{C{=}O}))/2$, was used in the correlation analysis as the most suitable IR spectroscopic parameter. The results of the statistical evaluation of the linear correlations are summarized in Table 5. It is evident that the $\bar{\nu}$(C=O) values correlate significantly with the sum of *Hammett*'s substituent constants ($\Sigma\sigma$) as well as with the rate coefficients of the base-catalyzed ring fission (log k_2) determined at both 25°C and 45°C. The correlation of $\bar{\nu}$(C=O) with the enthalpies of activation ($\Delta H^{\ddagger}$) is, however, less significant. For the correlation analysis of theoretical data (AM1), the arithmetic means of the bond orders and the oxygen charge densities were used as defined in Eqs. (1) and (2) below.

$$\bar{P}(\mathrm{C{=}O}) = (P(\mathrm{C}^{(1)} = \mathrm{O}^{(11)} + P(\mathrm{C}^{(2)} = \mathrm{O}^{(11')}))/2 \tag{1}$$

$$\bar{q}(\mathrm{O}) = (q(\mathrm{O}^{(11)}) + q(\mathrm{O}^{(11')}))/2 \tag{2}$$

It can be seen from Table 5 that satisfactory correlations exist between the $\bar{\nu}$(C=O)values and the theory derived parameters $\bar{P}$(C=O) and $\bar{q}$(O). The *Coulson* charge densities exhibit in all cases somewhat better correlations results than the *Mulliken* ones. The logk_2 values of the alkaline ring fission also show good

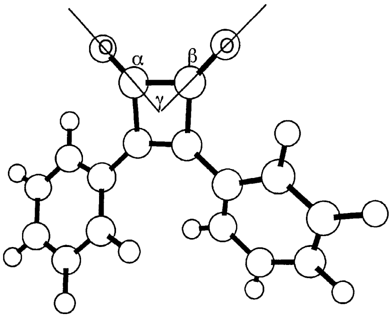
Table 5. Linear correlations for compounds **1–9** ($y = ax + b$)

y	x	r^{a}	s^{b}	F^{c}	a	b
$\bar{\nu}$(C=O)	$\Sigma\sigma$	0.955	0.62	72	5.14±0.60	1776.0
$\bar{\nu}$(C=O)	$\log k_2$ (25°C)	0.956	0.61	75	3.94±0.46	1769.0
$\bar{\nu}$(C=O)	$\log k_2$ (45°C)	0.957	0.60	76	4.31±0.49	1767.3
$\bar{\nu}$(C=O)	$\Delta H^{\ddagger}$	0.895	0.92	28	−1.85±0.35	1784.5
$\bar{\nu}$(C=O)	$\bar{P}$(C=O)	0.923	0.80	40	457.54±72.13	882.0
$\bar{\nu}$(C=O)	$\bar{q}(\mathrm{C{=}O})_{Couls}$	0.929	0.77	44	449.74±67.91	1874.2
$\bar{\nu}$(C=O)	$\bar{q}(\mathrm{C{=}O})_{Mull}$	0.899	0.91	30	428.79±78.90	1884.5
$\log k_2$ (25°C)	$\bar{P}$(C=O)	0.979	0.10	165	117.93±9.19	−228.51
$\log k_2$ (25°C)	$\bar{q}(\mathrm{O})_{Couls}$	0.973	0.12	125	114.47±10.24	26.79
$\log k_2$ (25°C)	$\bar{q}(\mathrm{O})_{Mull}$	0.972	0.12	121	112.63±10.23	30.29
$\log k_2$ (45°C)	$\bar{P}$(C=O)	0.982	0.09	184	108.13±7.97	−209.12
$\log k_2$ (45°C)	$\bar{q}(\mathrm{O})_{Couls}$	0.977	0.10	144	105.10±8.76	24.98
$\log k_2$ (45°C)	$\bar{q}(\mathrm{O})_{Mull}$	0.975	0.10	136	103.35±8.87	28.18
$\Delta H^{\ddagger}$	$\bar{P}$(C=O)	0.905	0.43	32	−216.79±38.60	427.94
$\Delta H^{\ddagger}$	$\bar{q}(\mathrm{O})_{Couls}$	0.887	0.46	26	207.55±40.94	−40.74
$\Delta H^{\ddagger}$	$\bar{q}(\mathrm{O})_{Mull}$	0.891	0.46	27	205.30±39.64	−47.36
ν_s (C=O)	ν_{as} (C=O)	0.941	0.89	54	1.069±0.145	−110.09

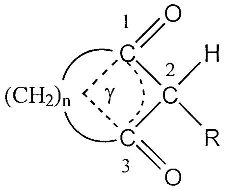
[a] Correlation coefficient; [b] standard deviation; [c] ratio of the correlation

correlations with AM1 results. Similar correlations of $\Delta H^{\ddagger}$ values with AM1 parameters are somewhat poorer compared to those of $\log k_2$. The former results support the conclusions of the mechanistic study of the base-catalyzed ring fission of the diones, *i.e.* that reaction occurs by addition of a hydroxide anion to the dione followed by the rate determining formation of a cyclopropene intermediate [5]. The sign and magnitude of the slope is as expected for the formation of the intermediates concerned. Finally, a good linear correlation was found between the wave numbers of the symmetric and those of the asymmetric C=O stretching vibrations for all compounds. Such a behaviour is similar to that of cyclic 1,3-diketones [16–20] which give statistically significant ν_s (C=O) *vs.* ν_{as} (C=O) dependences. As has been shown [18], the slope of the latter dependence and be interpreted as a measure of the symmetry of structural effects upon the wave numbers of the two vibrational modes ν_s (C=O) and ν_{as} (C=O) in the mechanically coupled cyclic dicarbonyl system. In the case of compounds **1**–**9**, the slope of the aforementioned correlation is approximately unity and demonstrates a symmetrical distribution of the structural effects and a strong cross-conjugation between the carbonyl groups and the substituted parts of the molecule.

Finally, we wish to discuss the monitoring of some geometrical properties of compounds **1**–**9** by infrared spectroscopic parameters. It has already been shown [19, 21] that the wave number separation of the absorption bands of symmetric and asymmetric C=O stretching vibrations ($\Delta\nu$(C=O)) in quasiplanar cyclic dicarbonyl systems can be considered as a measure of the vibrational coupling and should depend on the angle γ between the bond vectors of two C=O groups in the cyclic dicarbonyl system (Scheme 2). The $\Delta\nu$(C=O) values for various cyclic dicarbonyl compounds (**10**–**15**) together with the angles γ (see Scheme 3) are listed in Table 6.



Scheme 2



	R	*n*	other groups
10	H	5	-
11	H	4	-
12	C_6H_5	3	5-CH_3
13	H	2	-
14	CH_3	2	-
15	H	1	-

Scheme 3

Table 6. IR spectroscopic results in CCl_4 (cm^{-1}) and angles $\gamma(°)$ for cyclic dicarbonyl compounds **5**, **10–15**

	ν_s (C=O)	ν_{as} (C=O)	$\Delta\nu$(C=O)	Ref.	γ
5	1783.2	1776.9	6.3	this work	83[a], 93[b]
10	1708.1	1699.0	9.1	this work	89[c]
11	1723.5	1706.0	17.5	[19]	102[c]
12	1726.0	1697.0	29.0	[21]	132[d]
13	1751.0	1718.0	33.0	[22]	144[c]
14	1768.0	1729.0	39.0	[21]	149[d]
15	1809.0	1754.0	55.0	[21]	180[d]

[a] Predicted from the $\Delta\nu$ (C=O) *vs.* γ dependence (see Fig. 1 and Eq. (3)); [b] determined from AM1 results for optimized geometry; [c] calculated using molecular mechanics; [d] calculated from equation $A_{as}/A_s = \mathrm{tg}^2\gamma/2$ [21]

The linear dependence of $\Delta\nu$(C=O) (determined in CCl_4) on γ is demonstrated in Fig. 1 and can be expressed by the following empirical equation:

$$\Delta\nu(\mathrm{C{=}O}) = 0.485\gamma - 33.447 \tag{3}$$

For the parent compound **5**, $\Delta\nu$(C=O) determined in CCl_4 is 6.3 cm^{-1} which, according to the $\Delta\nu$(C=O) *vs.* γ correlation, corresponds to $\gamma = 83°$. This value is

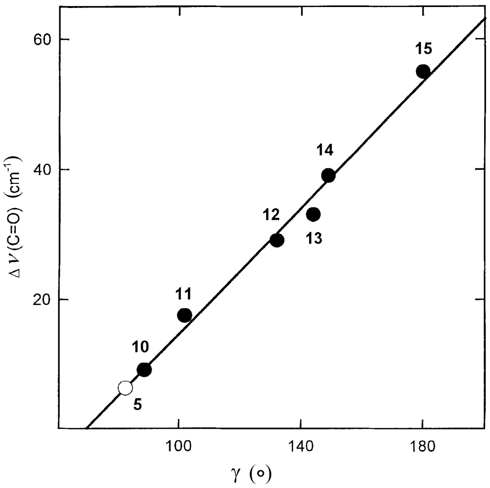


Fig. 1. Dependence of $\Delta\nu$(C=O) (in CCl_4) on the angle γ between the directions of the C=O bonds for various cyclic dicarbonyl compounds (**5**, **11–15**)

comparable to $\gamma = 93°$ as obtained from AM1 calculations (see Table 2). This shows that the geometry of the C=O bonds in 3,4-diphenylcyclobut-3-ene-1,2-dione (**5**) resembles that of cyclooctane-1,3-dione (**10**). Finally, it can be concluded that some geometrical properties of cyclic dicarbonyl compounds can be advantageously predicted or estimated using a combination of their spectroscopic and theoretical characteristics.

Experimental

The preparation and purification of compounds **1–9** has been described previously [1, 5].

The infrared spectra were measured at room temperature in the regions of 1800–1650 cm^{-1} and 1000–700 cm^{-1} using a Zeiss Specord M 80 spectrometer. The measurements were carried out in $CHCl_3$ and CCl_4 employing NaCl cells of 0.1 mm, 1.0 mm, and 2.5 mm thickness. $CHCl_3$ and CCl_4 were of spectral purity (Uvasol, Merck). The concentration of the solution in $CHCl_3$ for measurements in the region of 1800–1650 cm^{-1} was $4 \cdot 10^{-3}$ mol · dm^{-3}. In the other cases, the cocentrations were chosen to reach a maximum of absorption of 75–80%. Peak positions were determined with an accuracy of ±0.2 cm^{-1} against polystyrene standard spectra after mathematical deconvolution and separation of overlapping bands in the region of 1820–1710 cm^{-1}.

^{13}C NMR spectra were measured at 25°C using a Varian VXR 300 instrument operating at 75.429 MHz; solutions in $CDCl_3$ were used with tetramethylsilane as an internal standard.

The rate coefficients (k_2) and enthalpies of activation ($\Delta H^{\ddagger}$) of the base-catalyzed ring fission of the diones were determined in 50% (v/v) aqueous *DMSO* [5].

All computations were performed using the semiempirical AM1 (23] *Hamiltonian* as implemented in the VAMP [24] program package. Geometries were completely optimized (keyword PRECISE) using the eigenvector following routine [25]. Charges were obtained from *Mulliken* population analysis. Starting structures for all compounds were created by the SYBYL molecular modelling package [26]. For the definition of the angle γ, see Scheme 2.

Acknowledgements

The authors appreciate financial supports from the Scientific Grant Agency of the Ministry of Education of the Slovak Republic (grant No VEGA-1/4000/97), British Council in Bratislava (*Academic Link* between Colchester and Bratislava), and BAMO in Vienna (*Action Austria-Slovakia* in 1997). The molecular mechanistic calculations for compounds **10**, **11**, and **13** performed by Dr. *D. Loos* (Institute of Chemistry, Faculty of Natural Sciences, Comenium University, Bratislava) are gratefully acknowledged.

References

[1] Blomquist AT, Lalancette EA (1961) J Am Chem Soc **83**: 1387
[2] Hrnčiar P (1990) Organická chémia. SPN Bratislava, p 561
[3] Hine NG (1971) Chem Ber **104**: 2869
[4] Horák M, Papoušek D (1976) Infračervená Spektra a Struktura Molekul. Academia, Prague, p 684
[5] Al-Najjar A, Bowden K, Horri MV (1997) J Chem Soc Perkin Trans 2, 993
[6] Dchmolow EV, Zeisberg R (1975) Org Magn Res **7**: 418
[7] Bowden K, Agnihotri K, Ranson RJ, Perjéssy A, Hrnčiar P, Prokeš I, Fabian WMF (1997) J Phys Org Chem **10**: 841
[8] Perjéssy A, Hrnčiar P, Šusteková Z, Bowden K, Ranson RJ, Hritzová O, Prónayová N (1998) J Organomet Chem **552**: 1
[9] Bowden K, Ranson RJ, Perjéssy A, Lácová M, Hritzová O, Fabian WMF (1998) J Phys Org Chem **11**: 467
[10] Kolehmainen E, Lappalainen K, Tamminen J, Perjéssy A, Hrnčiar P, Lácová M, Fabian WMF (1998) Magn Res Chem **36**: 511
[11] Uhrin D, Liptaj T (1989) J Magn Res **81**: 82
[12] Hansch C, Leo A (1981) Substituent Constants for Correlation Analysis in Chemistry and Biology. Wiley, New York
[13] Perjéssy A, Hrnčiar P, Krutošíková A (1972) Tetrahedron **28**: 1025
[14] Perjéssy A, Hrnčiar P, Frimm R, Fišera L (1972) Tetrahedron **28**: 3781
[15] Perjéssy A, Hrnčiar P, Sokolová R (1973) Collect Czech Chem Commun **38**: 559
[16] Perjéssy A, Rotbergs J, Oškája VP (1976) Collect Czech Chem Commun **41**: 2209
[17] Perjéssy A, Hrnčiar P (1971) Tetrahedron **27**: 6159
[18] Perjéssy A, Hrnčiar P (1972) Collect Czech Chem Commun **37**: 1706
[19] Perjéssy A, Hrnčiar P, Šraga J (1983) Collect Czeck Chem Commun **48**: 586
[20] Perjéssy A, Szemes F, Hrnčiar P (1978) Acta Fac Univ Comen Chimia **36**: 73
[21] Fayat C, Faucaud A (1970) Bull Soc Chim Fr 4491
[22] Gren EJ, Vanag GJ (1960) Dokl Akad Nauk SSSR **133**: 588
[23] Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) J Am Chem Soc **107**: 3902
[24] Clark T (1992) VAMP Erlangen Vectorised Molecular Orbital Package, Version 4.40, Computer-Chemie-Zentrum, University Erlangen-Nürnberg, Germany
[25] Baker J (1986) Comput Chem **7**; 385
[26] SYBYL 6.2, Tripos Associates, St. Louis, MO

Received August 10, 1998. Accepted (revised) September 29, 1998