

Wavenumbers of C=O stretching vibrations of *exo*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide derivatives

^aA. PERJÉSSY and ^bE. SIDÓOVÁ

^aDepartment of Organic Chemistry, Faculty of Natural Sciences,
Komenský University, CS-842 15 Bratislava

^bInstitute of Chemistry, Komenský University,
CS-842 15 Bratislava

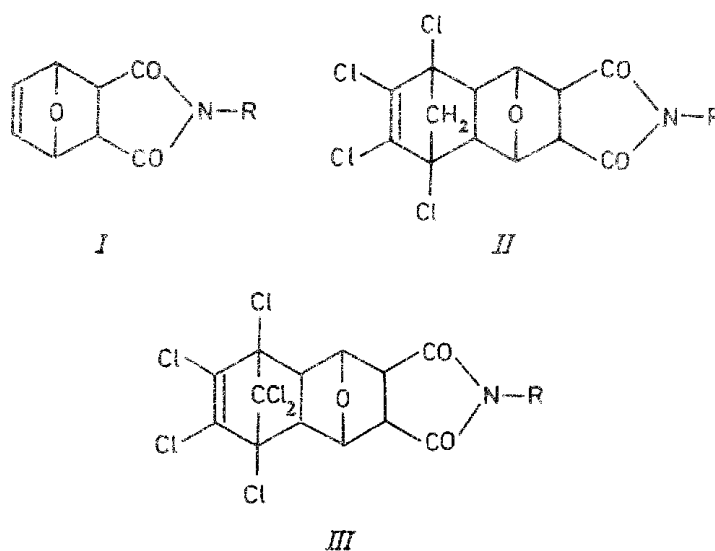
Received 11 May 1984

The wavenumbers of symmetric and antisymmetric C=O stretching vibrations were measured for 46 derivatives of *exo*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide in dilute solutions of tetrachloromethane and trichloromethane. A statistically significant correlation has been found between the wavenumbers of symmetric and antisymmetric C=O stretching vibrations in the series of 87 experimental points obtained for values measured in both solvents. The relation between the slope of $\tilde{\nu}_s(\text{C}=\text{O})$ vs. $\tilde{\nu}_{as}(\text{C}=\text{O})$ dependence and the structure of investigated compounds is discussed and compared with those for other five-membered cyclic imides and 1,3-dicarbonyl compounds.

Измерены волновые числа симметричных и асимметричных валентных колебаний связи C=O для 46 производных экзо-7-оксабицикло[2.2.1]гептан-2,3-дикарбоксимида в разбавленных растворах тетрахлорметана и трихлорметана. Обнаружена статистически значимая корреляция между волновыми числами симметричных и асимметричных валентных колебаний связи C=O для набора 87 экспериментальных точек, полученных для величин, измеренных в обоих растворителях. Обсуждается взаимосвязь между наклоном прямой, выражающей зависимость между $\tilde{\nu}_s(\text{C}=\text{O})$ и $\tilde{\nu}_{as}(\text{C}=\text{O})$ и структурой исследуемых соединений. Проведено сравнение с другими пятичленными циклическими имидами и 1,3-дикарбонильными соединениями.

Recently [1] the wavenumbers of maleimide derivatives were studied. Fayat and Foucaud [2] investigated particularly the wavenumbers of C=O stretching vibrations of various saturated cyclic dicarboximides. The wavenumbers of antisymmetric C=O stretching vibration measured in dioxan for seven derivatives of *N*-phenyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide were reported by Augustin *et al.* [3].

The present paper is connected with our previous communication [1] and belongs to our general and systematic study of C=O stretching vibrations of cyclic dicarbonyl compounds [4—11]. The aim of this work was to investigate the wavenumbers of C=O stretching vibrations for series of *exo*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximides *I—III*, which have been synthesized as compounds possessing biological activity [12—16] (Scheme 1).



Scheme 1

Experimental

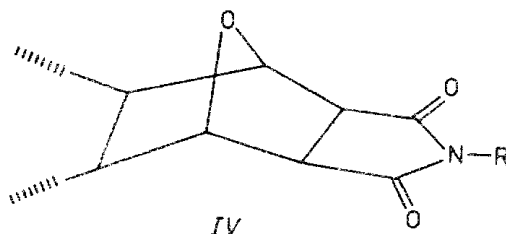
The preparation and properties of compounds *I* have been published [12—14] and compounds *II* and *III* were synthesized according to procedures reported before [15, 16]. All substances were purified before use for spectral measurements according to methods described [12—16].

The infrared spectra of compounds *I—III* were measured on a (Zeiss, Jena) Specord 75 IR spectrophotometer using solutions in tetrachloromethane and trichloromethane. For measurements of bands belonging to the antisymmetric C=O stretching vibration NaCl cells of 1 mm thickness were used. The less intense absorption bands of symmetric C=O stretching vibration were measured in 5 mm or 10 mm NaCl cells. Concentration of solutions in the range of 10^{-1} — 10^{-2} mol dm⁻³ was used to obtain 70—75 % maximal absorption of investigated bands. The wavenumber scale of the instrument was calibrated against the standard spectra of atmospheric water vapour and indene. The peak positions were determined from three measurements with an accuracy ± 0.5 cm⁻¹.

Results and discussion

As the syntheses of all investigated 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximides [12—16] started from *exo*-isomers of corresponding cyclic anhydrides it can

be supposed that compounds *I—III* have also an *exo* configuration of the 2,3-dicarboximide ring with respect to the oxygen atom in position 7 (*IV*) (Scheme 2). Generally the *exo*-isomers of 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide



Scheme 2

are more stable than the corresponding *endo*-isomers, which owing to the light easily change for *exo*-isomers [17, 18].

Similarly to other cyclic imides derivatives of 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide *I—III* exhibit in the regions of $\tilde{\nu} = 1710\text{—}1746\text{ cm}^{-1}$ and $\tilde{\nu} = 1775\text{—}1808\text{ cm}^{-1}$ two absorption bands. The more intense band at lower values of $\tilde{\nu}$ belongs to the antisymmetric stretching vibration, $\nu_{as}(\text{C}=\text{O})$, while the band at higher values of $\tilde{\nu}$ and with a lower intensity can be assigned to the symmetric stretching vibration, $\nu_s(\text{C}=\text{O})$, of the vibrationally coupled CONCO system of the imide ring. The wavenumbers of both the symmetric and antisymmetric C=O stretching vibrations measured in CCl_4 and CHCl_3 for compound series *I—III* are given in Table 1. The values of $\tilde{\nu}_s(\text{C}=\text{O})$ and $\tilde{\nu}_{as}(\text{C}=\text{O})$ for compounds *I—III* are similar to those observed [2] in the case of analogous saturated five-membered cyclic imides, *i.e.* succinimides ($\tilde{\nu}_s(\text{C}=\text{O}) = 1781\text{—}1801\text{ cm}^{-1}$ and $\tilde{\nu}_{as}(\text{C}=\text{O}) = 1708\text{—}1735\text{ cm}^{-1}$).

The degree of vibrational coupling in CONCO system, which can be expressed as the difference between the wavenumbers of symmetric and antisymmetric C=O stretching vibrations, $\Delta\tilde{\nu} = \tilde{\nu}_s(\text{C}=\text{O}) - \tilde{\nu}_{as}(\text{C}=\text{O})$ [2, 19, 20] for compounds *I—III* is observed in the region of $58\text{—}67.5\text{ cm}^{-1}$ and is similar to values in the case of derivatives of succinimide ($\Delta\tilde{\nu} = 54\text{—}74\text{ cm}^{-1}$) [2] and maleimide ($\Delta\tilde{\nu} = 51\text{—}66\text{ cm}^{-1}$) [1]. The comparison with five-membered cyclic 1,3-diketones ($\Delta\tilde{\nu} = 35\text{—}50\text{ cm}^{-1}$) [4, 9] shows that the degree of vibrational coupling is much higher in cyclic imides. This is connected with the change in geometry of the five-membered ring on replacing the carbon atom in position 2 by nitrogen atom, as well as with a partially sp^2 character of the imide ring C—N bond.

Compounds of the series *I—III*, like maleimides [1] and various five-membered 1,3-diketones [4, 7—11], exhibit a linear correlation between the wavenumbers of symmetric and antisymmetric C=O stretching vibrations. As the experimental values measured in both solvents CCl_4 and CHCl_3 for all three series *I—III* fall in the same correlation $\tilde{\nu}_s(\text{C}=\text{O})$ vs. $\tilde{\nu}_{as}(\text{C}=\text{O})$, the data given in Table 1 for 87

Table 1

Wavenumbers of symmetric and antisymmetric C=O stretching vibrations for derivatives of *exo*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide of series I—III

Compound No.	R ^a	$\bar{\nu}/\text{cm}^{-1}$			
		CCl ₄		CHCl ₃	
		$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$	$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$
Series I					
1	OH	<i>b</i>	<i>b</i>	1786	1718
2	Oi-Pr	1792	1729	1789.5	1724
3	OCH=CH ₂	1793	1732	1790	1726.5
4	OHept	1793	1732	1790	1725
5	OCHMeEt	1791.5	1729	1789	1722.5
6	OCH ₂ CH=CMeCl	1793.5	1732.5	1790.5	1726.5
7	Oi-Pe	1792	1732	1790	1724.5
8	Oc-Pe	1791.5	1730	1788.5	1723.5
9	OCH ₂ Ph	1792.5	1731.5	1790.5	1726
10	OCOMe	1790	1723	1786	1721.5
11	OCOPh	1808	1746	1805	1740
12	NHPh	1786.5	1729.5	1790	1727.5
13	NH[2,4-(NO ₂) ₂ Ph]	1795	1732.5	1797.5	1739.5
14	NHCOMe	<i>b</i>	<i>b</i>	1797.5	1735
15	N(COMe) ₂	1802	1735.5	1799.5	1742
16	NHCOCH ₂ Ph	<i>b</i>	<i>b</i>	1798	1737
17	NHCOPh	<i>b</i>	<i>b</i>	1798	1737
18	NHCO(2-Fu)	<i>b</i>	<i>b</i>	1800	1738.5
19	N=CHPh	1785.5	1720.5	1780.5	1716
20	N=CH(4-NMe ₂ Ph)	1780	1714.5	1775.5	1710.5
21	N=CH(2-OHPh)	1789	1724.5	1785	1720
22	N=CH(2-ClPh)	1787	1723.5	1782	1719.5
23	N=CH(4-ClPh)	1786.5	1721.5	1781.5	1716.5
24	N=CH(2-NO ₂ Ph)	1788	1726	1783.5	1721
25	N=CH(3-NO ₂ Ph)	1786.5	1724	1784	1720
26	N=CH(4-NO ₂ Ph)	1790	1726	1785.5	1720.5
27	N=CH(2-Fu)	1787	1720.5	1781	1717
Series II					
28	OMe	1796	1736	1794.5	1731.5
29	OEt	1796	1736.5	1792	1730
30	OPr	1795.5	1736.5	1792	1730
31	Oi-Pr	1795	1734	1790.5	1728.5
32	OCH ₂ CH=CH ₂	1796	1737.5	1792.5	1730
33	OCHMeEt	1795.5	1736.5	1791	1728.5
34	OCH ₂ CH=CMeCl	1796	1736.5	1792.5	1729.5
35	Oi-Pe	1796	1736	1792	1729.5

Table 1 (Continued)

Compound No.	R ^a	$\tilde{\nu}/\text{cm}^{-1}$			
		CCl ₄		CHCl ₃	
		$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$	$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$
36	OCH ₂ Ph	1796	1736.5	1792	1730.5
Series III					
37	OH	1786	1721.5	1790	1722.5
38	OMe	1797.5	1736.5	1795	1732.5
39	OEt	1795.5	1737.5	1794.5	1731
40	OPr	1796.5	1737	1794	1731
41	Oi-Pr	1797	1737	1792.5	1730
42	OCH ₂ CH=CH ₂	1798	1738	1794	1731
43	OBu	1796.5	1737	1793.5	1730.5
44	OCHMeEt	1796.5	1736	1792	1729.5
45	OCH=CMeCl	1797	1738.5	1793.5	1730.5
46	Oc-Pe	1796	1737	1792	1729

a) The abbreviations used in denoting the substituents R: Pr — propyl, Hept — heptyl, Et — ethyl, i-Pe— isopentyl, c-Pe—cyclopentyl, Ph—phenyl, Me—methyl, 2-Fu—2-furyl, i-Pr— isopropyl, Bu—butyl.

b) Insoluble in CCl₄.

experimental points can be evaluated statistically by a single dependence (eqn (1)) illustrated in Fig. 1.

$$\tilde{\nu}_s(\text{C}=\text{O}) = (0.747 \pm 0.025) \cdot \tilde{\nu}_{as}(\text{C}=\text{O}) + (499.895 \pm 43.316) \text{ cm}^{-1} \quad (1)$$

$$r = 0.955 \quad s = 1.648 \text{ cm}^{-1}$$

where r is the correlation coefficient and s the standard deviation of dependence (eqn (1)).

A more detailed analysis of statistical results of correlation reveals that only 5.7 % of experimental points deviate by ± 3.0 — 5.6 cm^{-1} from the estimated straight line and the deviation of 86.2 % of the experimental points is less than $\pm 2 \text{ cm}^{-1}$. It follows from the above-mentioned results that eqn (1) is statistically significant and can be compared to analogical relationships found for other similar systems.

It has been already shown in preceding papers [2, 8, 10, 11] that the slope ρ of $\tilde{\nu}_s(\text{C}=\text{O})$ vs. $\tilde{\nu}_{as}(\text{C}=\text{O})$ dependence expresses the symmetry of separation of structural effects upon the wavenumbers of two vibrational modes of mechanically coupled system and its value depends on direct conjugation between the vibrating

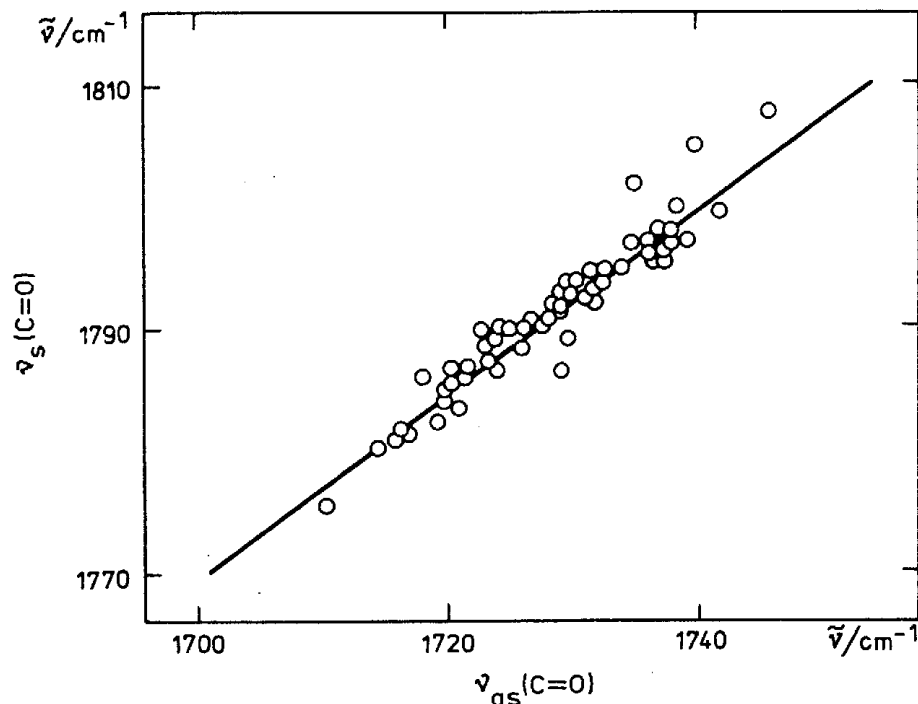


Fig. 1. Relationship between the wavenumbers of symmetric and antisymmetric C=O stretching vibrations for derivatives of *exo*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide I—III.

C=O groups. For systems in which such a conjugation is absent, e.g. for saturated cyclic 1,3-diketones [2, 11], the value of ρ is close to 1. In the case of aromatic or unsaturated cyclic 1,3-dicarbonyl compounds [4, 8—10] the value of ρ decreases depending on the number of electrons contributing to the resonance interaction between the C=O bonds. The value of slope of $\tilde{\nu}_s(\text{C}=\text{O})$ vs. $\tilde{\nu}_{as}(\text{C}=\text{O})$ correlation observed for succinimide derivatives is very low ($\rho \sim 0.6$), because the system is conjugated directly through the lone electron pair of nitrogen atom located between the two C=O groups. An evidence of this is also the fact that in series of saturated *N*-substituted cyclic 2,3-dicarboximides the substituents influence significantly the wavenumbers of antisymmetric C=O stretching vibration [3]. In the case of maleimides [1] the π -electrons of C=C bond play a substantial role in conjugation between the C=O groups and consequently the value of slope of the above-mentioned dependence increases to $\rho = 0.93$.

For derivatives of *exo*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide studied herein the value of the slope of $\tilde{\nu}_s(\text{C}=\text{O})$ vs. $\tilde{\nu}_{as}(\text{C}=\text{O})$ dependence ($\rho = 0.75$) is somewhat higher than the value of ρ observed in the case of succinimide derivatives. This can be explained as a weakening of resonance interaction between the C=O groups resulting probably from the break of coplanarity in the five-membered imide ring owing to its *exo* configuration (IV) with respect to oxygen atom in position 7 (Scheme 2).

On the basis of these results the conclusion can be drawn that also the structure of farther cycle fused to five-membered ring of saturated 2,3-dicarboximides influences the symmetry of separation of structural effects upon the $\tilde{\nu}_s$ and $\tilde{\nu}_{as}$ values as well as the conjugation between the vibrating C=O groups.

Acknowledgements. Our thanks are due to Dr. V. Blanáriková and Z. Šusteková (Institute of Chemistry, Komenský University, Bratislava) for technical assistance.

References

1. Perjéssy, A., Augustin, M., and Köhler, M., *Collect. Czechoslov. Chem. Commun.* 50, 1305 (1985).
2. Fayat, C. and Foucaud, A., *Bull. Soc. Chim. Fr.* 1970, 4491.
3. Augustin, M., Köhler, M., and Härtling, S., *J. Prakt. Chem.* 315, 717 (1973).
4. Perjéssy, A. and Hrnčiar, P., *Tetrahedron* 27, 6159 (1971).
5. Perjéssy, A., Hrnčiar, P., and Krutošíková, A., *Tetrahedron* 28, 1025 (1972).
6. Perjéssy, A., Hrnčiar, P., and Fišera, L., *Tetrahedron* 28, 3781 (1972).
7. Perjéssy, A., Hrnčiar, P., and Sokolová, R., *Collect. Czechoslov. Chem. Commun.* 38, 559 (1973).
8. Perjéssy, A., Rotbergs, J., and Oškāja, V. P., *Collect. Czechoslov. Chem. Commun.* 41, 2209 (1976).
9. Perjéssy, A., Temkovitz, P., and Hrnčiar, P., *Collect. Czechoslov. Chem. Commun.* 41, 2904 (1976).
10. Perjéssy, A., Szemes, F., and Hrnčiar, P., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* 26, 73 (1978).
11. Perjéssy, A., Hrnčiar, P., and Šraga, J., *Collect. Czechoslov. Chem. Commun.* 48, 586 (1983).
12. Sidóová, E., *Chem. Zvesti* 27, 122 (1973).
13. Sidóová, E., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* 16, 49 (1971).
14. Furdík, M., Sidóová, E., and Priehradný, S., *Chem. Zvesti* 19, 611 (1965).
15. Sidóová, E., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* 18, 33 (1973).
16. Sidóová, E., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* 19, 109 (1974).
17. Vaughan, W. E., *J. Amer. Chem. Soc.* 54, 3863 (1932).
18. Vaughan, W. E., *J. Amer. Chem. Soc.* 55, 4109 (1933).
19. Bellamy, L. J., Conelly, B. R., Philpotts, A. R., and Williams, R. L., *Z. Electrochem.* 64, 563 (1960).
20. Mecke, R. and Funck, E., *Z. Elektrochem.* 60, 1124 (1956).

Translated by A. Perjéssy