

WAVENUMBERS OF C=O VALENCE VIBRATIONS OF ENDO-BICYCLO[2.2.1]HEPT-5-ENE-2,3-DICARBOXIMIDES

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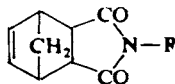
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Wavenumbers of symmetrical and antisymmetrical C=O valence vibrations of 50 derivatives of endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide have been measured in tetrachloromethane and chloroform. A satisfactory linear correlation between $\nu_s(\text{C}=\text{O})$ and $\nu_{as}(\text{C}=\text{O})$ has been found for 98 experimental points obtained in the two solvents. The anomalous low slope value $\rho = 0.43$ of this dependence can be used as evidence for endo configuration of the bicyclic 2,3-dicarboximides. The results are discussed in comparison with analogous relations found for other five-membered cyclic dicarboximides.

In previous papers¹⁻³ we studied wavenumber of C=O valence vibrations of a series of maleinimides and some bicyclic 2,3-dicarboximides. Fayat and Foucaud⁴ studied in detail relations between infrared spectra and structure of saturated five-membered cyclic imides. Augustin and coworkers⁵ correlated the wavenumbers of antisymmetrical C=O valence vibrations measured in tetrahydrofuran for some substituted N-phenylbicyclo[2.2.1]-hept-5-ene-2,3-dicarboximides with the corresponding Hammett σ constants.

The aim of the present communication, which forms a continuation of the earlier studies¹⁻⁵, was investigation of relation between symmetrical and antisymmetrical C=O valence vibrations of a greater number of derivatives of endo-bicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide of general formula *I* and comparison of the results with analogous relations obtained so far for other five-membered cyclic imides.



I

EXPERIMENTAL

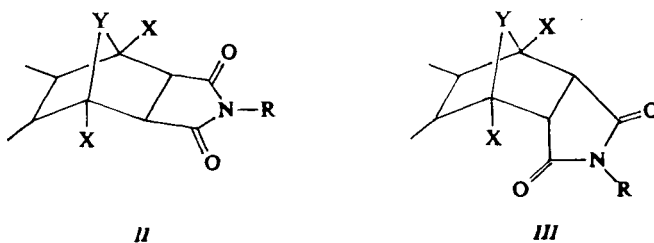
Preparation and some properties of the bicycloheptenedicarboximides *I* are described elsewhere⁶⁻¹⁰ except for compounds Nos 3, 39, 40, 48, 50 (Table I). N-(4-Thiocyanatophenyl)-

bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (compound No 48) was prepared according to ref.⁵, preparation of compounds 3, 39, 40, and 50 has not been published yet¹¹.

The IR spectra of the compounds *I* were measured in CCl₄ and CHCl₃ solutions using a Zeiss Specord model 75 IR. For the measurements of wavenumbers of antisymmetrical C=O valence vibration we used 1 mm NaCl cells. The less intensive absorption bands of symmetrical C=O valence vibration were measured in 5 or 10 mm cells. Concentration of the solutions was chosen in such way that intensity of the bands studied reached 70–75% of the maximum absorption. The wavenumber scale of the apparatus was calibrated with the use of reference spectrum of atmospheric water vapour and indene. Position of the absorption bands was determined with the accuracy of $\pm 0.5 \text{ cm}^{-1}$ as arithmetic mean of three measurements.

RESULTS AND DISCUSSION

The 2,3-dicarboximides of seven-membered bicyclic derivatives can exist in two possible configurations, *exo* (*II*) or *endo* (*III*), with respect to mutual spatial arrangement of the five-membered imidic ring and the bridge group at 7 position of the bicyclic skeleton.



1,4,5,6-Tetrachloro-, 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hept-5-ene-2,3-dicarboximides and derivatives of 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide, which were studied in the previous works^{2,3}, had the *exo* configuration *II* (X = Cl, Y = CH₂, CCl₂, and X = H, Y = O, respectively). On the basis of structure of the starting materials in the syntheses, *endo* configuration *III* (X = H, Y = CH₂) was assigned^{6–11} to the derivatives of bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide *I* which are dealt with in the present paper.

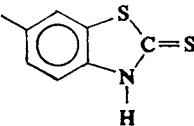
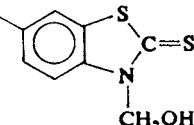
The wavenumbers of symmetrical $\nu_s(\text{C}=\text{O})$ and antisymmetrical valence vibration $\nu_{as}(\text{C}=\text{O})$ of the *endo* isomers of bicycloheptenedicarboximides *I* are found in the regions $1788\text{--}1770 \text{ cm}^{-1}$ and $1738\text{--}1696 \text{ cm}^{-1}$, respectively (Table I). The said absorption region of compounds *I* is lower than that of the *exo* isomers of 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximides and chloro derivatives of bicyclohept-5-ene-2,3-dicarboximides³. Anomalously high wavenumber values of the mentioned chloro derivatives ($\nu_s(\text{C}=\text{O}) = 1820\text{--}1784 \text{ cm}^{-1}$ and $\nu_{as}(\text{C}=\text{O}) = 1763\text{--}1721 \text{ cm}^{-1}$), as compared with the *endo* isomers of compounds *I*, can be explained by non-bonding interactions between the vibrating C=O bonds and C—Cl bonds which

TABLE I

Wavenumbers (in cm^{-1}) of $\text{C}=\text{O}$ valence vibrations of derivatives of *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (*I*)

Compound No	R^a	CCl_4		CHCl_3	
		$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$	$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$
1	Me	1 767.5	1 733	1 763.5	1 725.5
2	Et	1 775	1 703	1 771	1 695.5
3	C_5H_7^b	1 770	1 704	1 765.5	1 696.5
4	OH	1 782	1 721	1 778.5	1 711.5
5	OMe	1 785.5	1 730.5	1 783	1 723.5
6	OEt	1 785.5	1 730	1 781.5	1 722.5
7	OPr ⁱ	1 783.5	1 729	1 781	1 720
8	$\text{OCH}_2\text{CH}=\text{CH}_2$	1 784	1 730	1 782	1 722
9	$\text{OCH}_2\text{CH}=\text{CMeCl}$	1 784	1 729.5	1 781.5	1 723.5
10	OCH_2Ph	1 783	1 729.5	1 780.5	1 724
11	OCH_2COOMe	1 786	1 734	1 784	1 729
12	$\text{OCH}_2\text{CONHOct}$	1 784	1 728.5	1 782.5	1 725.5
13	$\text{C}_5\text{H}_{10}\text{N}^c$	1 784.5	1 732.5	1 783	1 728
14	$\text{C}_4\text{H}_8\text{NO}^d$	1 784.5	1 733.5	1 782.5	1 728.5
15	$\text{OCH}_2\text{CONHPh}$	1 785	1 732	1 783	1 725
16	$\text{OCH}_2\text{CONH}(2\text{-NO}_2\text{Ph})$	1 787	1 738	1 784.5	1 731
17	OCOCH_2Ph	1 784.5	1 736.5	1 783	1 737.5
18	$\text{OCO}(2\text{-ClPh})$	1 784	1 735.5	1 782	1 737.5
19	$\text{OCO}(2\text{-Fu})$	1 784.5	1 736	1 777	1 738
20	NH_2	1 776.5	1 707.5	1 777.5	1 705
21	$\text{N}=\text{CHPh}$	1 775	1 716	1 770.5	1 712.5
22	$\text{N}=\text{CH}(2\text{-OHPh})$	1 779	1 721	1 775	1 715.5
23	$\text{N}=\text{CH}(2\text{-ClPh})$	1 774.5	1 720	1 772	1 714.5
24	$\text{N}=\text{CH}(4\text{-ClPh})$	1 780	1 719	1 773	1 715
25	$\text{N}=\text{CH}(2\text{-NO}_2\text{Ph})$	1 777	1 722.5	1 772.5	1 714.5
26	$\text{N}=\text{CH}(3\text{-NO}_2\text{Ph})$	1 777.5	1 721	1 773.5	1 715.5
27	$\text{N}=\text{CH}(2\text{-Fu})$	1 778	1 719.5	1 774	1 713.5
28	6-(2-SMeBT)	1 780.5	1 719.5	1 773	1 711.5
29	6-(2-SEtBT)	1 779.5	1 719	1 773	1 711
30	6-(2-SPr ⁱ BT)	1 780	1 720	1 773	1 711
31	6-(2-SCH ₂ CH=CH ₂ BT)	1 780.5	1 719.5	1 772.5	1 711
32	6-(2-SBu ⁱ BT)	1 779	1 719	1 773	1 711.5
33	6-(2-SCHMeEtBT)	1 780	1 719.5	1 774.5	1 711
34	6-(2-SPe ⁱ BT)	1 779.5	1 718	1 773	1 711
35	6-(2-SPe ^c BT)	1 779.5	1 717.5	1 773.5	1 711.5
36	6-(2-SC ₆ H ₉ BT) ^e	1 779.5	1 719.5	1 773	1 711
37	6-(2-SCH ₂ PhBT)	1 780.5	1 720	1 773	1 712
38	6-(2-SCH ₂ CH ₂ OHBT)	1 780	1 720	1 772.5	1 712
39	6-(2-SCH ₂ COOHBT)	1 780	1 720.5	1 772	1 713

TABLE I
(Continued)

Compound No	R ^a	CCl ₄		CHCl ₃	
		$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$	$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$
40	6-(2-SCH ₂ COOMeBT)	<i>f</i>	1 720.5	1 772	1 712
41	CH ₂ NH-6-(2-SMeBT)	1 773.5	1 706	1 771.5	1 700.5
42	CH ₂ NH-6-(2-SEtBT)	1 774	1 706	1 771	1 700
43	CH ₂ NH-6-(2-SPr ⁱ BT)	1 775	1 706.5	1 711	1 699.5
44	CH ₂ NH-6-(2-SCH ₂ CH=CH ₂ BT)	1 774	1 706.5	1 771	1 700
45	CH ₂ NH-6-(2-SBu ⁱ BT)	1 774	1 706.5	1 771	1 699
46	CH ₂ NH-6-(2-SCH ₂ PhBT)	1 775	1 706.5	1 771	1 700
47	CH ₂ NH-6-(2-SCH ₂ CH ₂ OHBT)	1 774.5	1 706.5	1 771.5	1 700
48	4-SCNPh	1 781.5	1 722	1 773.5	1 712.5
49		1 777	1 721	1 776	1 712
50		1 778	1 721	1 776	1 713

^a The abbreviations used for R substituents: Me methyl, Et ethyl, Prⁱ isopropyl, Ph phenyl, Oct octyl, 2-Fu 2-furyl, BT benzothiazolyl, Buⁱ isobutyl, Peⁱ isopentyl, Pe^c cyclopentyl. ^b 3-Cyclopentenyl. ^c Piperidino. ^d Morpholino. ^e C₆H₉ means 3-cyclohexenyl. ^f Overlap with the band of C=O valence vibration of COOMe group.

can make themselves felt only in exo configurations (*II*, X = Cl, Y = CH₂, CCl₂) of these compounds.

The wavenumber difference $\Delta\nu = \nu_s(\text{C}=\text{O}) - \nu_{as}(\text{C}=\text{O})$, which can – in other systems – be interpreted as a measure of vibrational coupling in the five-membered ring^{12–17}, is observed with the endo isomers *I* in a very broad interval of values: 44–75.5 cm⁻¹. This fact prevents quantitative comparison of the $\Delta\nu$ value of compounds *I* with similar values of other five-membered cyclic imides and its interpretation by geometrical structure of the compounds.

The compound *I* as well as other cyclic imides^{1–4} or 1,3-diketones^{14–17} give satisfactory linear correlations between wavenumbers of symmetrical and antisymmetrical C=O valence vibrations. As the values measured in the two solvents (CCl₄,

CHCl_3) lie at the same straight line, our correlation analysis involves all the data of Table I, *i.e.* 98 experimental points, with the following result:

$$\nu_s(\text{C}=\text{O}) = (0.430 \pm 0.021) \nu_{as}(\text{C}=\text{O}) + (1\,039.071 \pm 35.800) \quad (1)$$

$$r = 0.903, \quad s = 2.169,$$

where r is correlation coefficient and s means standard deviation. Excluded from the correlation were the wavenumbers of compound No 19 measured in CHCl_3 , because they deviated from the calculated linear dependence (1) more distinctly than the values of the other derivatives *I*. Also omitted were the data obtained for compound 40 in CCl_4 , because its absorption band of $\nu_{as}(\text{C}=\text{O})$ vibration is overlapped by that of $\text{C}=\text{O}$ valence vibration of COOCH_3 group of the substituent bound in side chain of the benzothiazole skeleton.

Figure 1 presents a statistical estimate of the linear dependence. A more detailed analysis of the results shows that only 16.3% of the experimental points (out of the total number) are deviated from the calculated straight line (1) by $5.1 - 3.0 \text{ cm}^{-1}$, whereas 83.7% of the points exhibit deviations smaller than 3 cm^{-1} . From these results and from the standard deviation of the slope $\varrho (\pm 0.021, \text{i.e. } 5\% \text{ of the } \varrho \text{ value})$ it can be concluded that the relation (1) is sufficiently statistically significant and allows further conclusions about structure of the compounds investigated.

Comparison of the slope value ($\varrho = 0.43$) of the linear dependence $\nu_s(\text{C}=\text{O})$ vs $\nu_{as}(\text{C}=\text{O})$ of the endo isomers of compounds *I* with analogous values obtained for exo isomers of 1,4,5,6-tetrachloro- and 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene

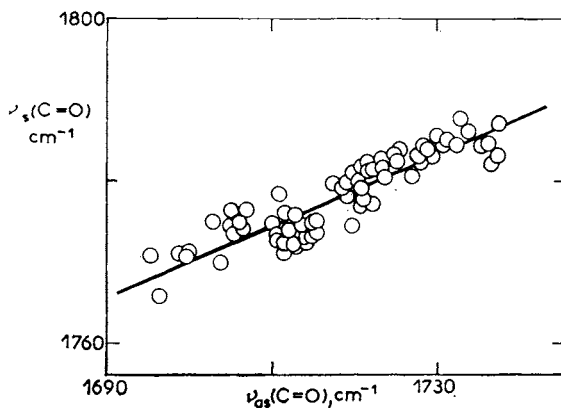


FIG. 1

Dependence between wavenumber of symmetrical and antisymmetrical $\text{C}=\text{O}$ valence vibrations of endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximides *I*

-2,3-dicarboximides³ ($\rho = 0.83$) and derivatives of 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide² ($\rho = 0.75$) shows that the former is smaller than the latter ones by almost 50%. It is noteworthy that such a low slope value of a dependence $\nu_s(\text{C=O})$ vs $\nu_{as}(\text{C=O})$ has not been observed yet with any other cyclic imides^{1,4} and with cyclic 1,3-dicarbonyl systems¹⁴⁻¹⁸. The anomalously low slope value (ρ) of the said dependence of the bicyclic 2,3-dicarboximides type *III* can thus be considered generally to represent evidence for endo configuration of these compounds.

In conclusion it can be stated that value of the ρ slope of the dependence $\nu_s(\text{C=O})$ vs $\nu_{as}(\text{C=O})$ is distinctly affected not only by electronic properties of bonds and geometry of the five-membered ring of cyclic imides but also by steric arrangement of the further cycle bound to this system, and, hence, it can provide valuable information on structure of these compounds.

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