

## THE WAVENUMBERS OF C=O STRETCHING VIBRATIONS OF MALEINIMIDES

Alexander PERJÉSSY<sup>a</sup>, Manfred AUGUSTIN<sup>b</sup> and Manfred KÖHLER<sup>b</sup>

<sup>a</sup> Department of Organic Chemistry,

Comenius University 842 15 Bratislava, Czechoslovakia and

<sup>b</sup> Department of Chemistry,

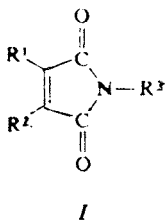
Martin Luther University, 4 020 Halle - Wittenberg, GDR

Received May 22nd, 1984

The infrared spectra in the region of fundamental C=O stretching vibrations in tetrachloromethane and chloroform were measured for 59 maleinimide derivatives. A linear correlation between the wavenumbers of symmetric and antisymmetric C=O stretching vibrations was found for a series of 102 experimental data obtained in both solvents. The slope of the  $\nu_s(\text{C}=\text{O})$  vs  $\nu_{as}(\text{C}=\text{O})$  dependence as well as the degree of the vibrational coupling in imide system were discussed and compared with those for analogical five-membered cyclic 1,3-diketones.

The C=O stretching vibrations of various saturated four-, five- and six-membered cyclic imides were investigated particularly by Fayat and Foucaud<sup>1</sup>. Augustin and co-workers<sup>2</sup> studied the antisymmetric C=O stretching vibration in tetrahydrofuran solution for series of saturated cyclic and bicyclic imides. The wave numbers of antisymmetric C=O stretching vibration of some derivatives of maleinimide measured in the solid state were reported by Augustin and Köhler<sup>3</sup>. Our previous papers<sup>4-15</sup> were devoted to the investigation of the C=O stretching vibrations of various series of cyclic 1,3-diketones. However, the C=O stretching vibrations of unsaturated cyclic imides have not yet been studied systematically.

In connection with our general investigation on infrared spectra and structure of dicarbonyl compounds we aimed this communication to study the C=O stretching vibrations of a series of maleinimide derivatives *I*.



## EXPERIMENTAL

The preparation and properties of compounds *I* (No 1–56, Table I) have been reported<sup>3,16,17</sup>. The synthesis of remaining maleinimides *I* (No 57–59, Table I) has not yet been published<sup>18</sup>.

The infrared spectra of  $\text{CCl}_4$  and  $\text{CHCl}_3$  solutions of compounds *I* were taken on a Zeiss, model 75 IR Specord spectrophotometer. The wave numbers of antisymmetric C=O stretching vibration were measured in NaCl cells of 1 mm thickness. The less intense absorption bands of symmetric C=O stretching vibration were obtained by measuring of solutions in NaCl cells of 5 or 10 mm thickness. Concentration of the solutions met requirement for a 70–75% absorption of the examined band maxima. The wavenumber scale of the instrument was calibrated against reference spectra of both indene and atmospheric water vapor. Peak positions were determined by averaging the results of three measurements and are believed to be accurate to  $\pm 0.5 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

Maleinimides (*I*) (Table I) analogously to other cyclic imides, anhydrides or 1,3-diketones exhibit in the regions of  $1830\text{--}1730 \text{ cm}^{-1}$  two absorption bands belonging to the symmetric ( $\nu_s(\text{C}=\text{O})$ ) and antisymmetric ( $\nu_{as}(\text{C}=\text{O})$ ) stretching vibrations of the coupled CONCO system. The  $\nu_{as}(\text{C}=\text{O})$  absorption bands are more intense than the  $\nu_s(\text{C}=\text{O})$  ones which is in agreement with other five-membered cyclic imides<sup>1–3</sup>. The wavenumbers of both the symmetric and antisymmetric C=O stretching vibrations of maleinimides *I* appeared at higher values when compared with unsaturated or aromatic five-membered cyclic 1,3-diketones<sup>4,9,12</sup>. This can be rationalized by the change of valence angles in five-membered ring as a result of the contraction of the ring size replacing the carbon atom by nitrogen one. The electron-withdrawing effect of the nitrogen atom in the imide ring plays also an important role in the increase of wavenumbers of both the  $\nu_s(\text{C}=\text{O})$  and  $\nu_{as}(\text{C}=\text{O})$  vibrations.

It has been shown<sup>1,19,20</sup> that the wavenumber separation between the symmetric and antisymmetric C=O stretching vibrations  $\Delta\nu = \nu_s(\text{C}=\text{O}) - \nu_{as}(\text{C}=\text{O})$  can be considered as a measure of the vibrational coupling in cyclic 1,3-dicarbonyl system and depends on the angle formed by two vibrating C=O bonds. For maleinimides *I* the  $\Delta\nu$  values were found in the range of  $51\text{--}66 \text{ cm}^{-1}$  which is successively higher than that observed for unsaturated or aromatic 1,3-diketones ( $\Delta\nu = 35$  to  $50 \text{ cm}^{-1}$ )<sup>4,9</sup>. The phenomenon of this is well explainable again by diminution of the ring size substituting the carbon atom linked on two C=O groups by nitrogen one. The smaller ring size of maleinimides causes an enlargement of the angle formed by two vibrating C=O bonds in comparison with that of unsaturated or aromatic cyclic 1,3-diketones.

Similarly to cyclic 1,3-diketones<sup>4,8–10,12</sup> also maleinimides *I* reveal a linear correlation between the wavenumbers of symmetric and antisymmetric C=O stretching vibrations. As all experimental values measured in both solvents  $\text{CCl}_4$  and  $\text{CHCl}_3$  lie practically on the same line, we evaluated the data by a common correlation

for 102 experimental points (Fig. 1):

$$\nu_s(\text{C=O}) = 0.925(\pm 0.027) \nu_{as}(\text{C=O}) + 185.971(\pm 47.251)$$

$$r = 0.925 \quad s = 3.232,$$

where  $r$  is the correlation coefficient and  $s$  the standard deviation. The values included in correlation are evident from the footnotes in the Table I. Data for some compounds were excluded from the correlation on account of their larger deviation from the straight line compared to the majority of experimental points. The particular statistical treatment showed that only 8.8% of experimental points deviated from the correlation by 5.0–7.5  $\text{cm}^{-1}$ , while the deviation of 91.2% of them was lower than 5  $\text{cm}^{-1}$ .

The slope of  $\nu_s(\text{C=O})$  vs  $\nu_{as}(\text{C=O})$  dependence ( $\rho = 0.92 \text{ cm}^{-1}$ ) is markedly higher compared to those of unsaturated and aromatic five-membered cyclic 1,3-diketones *II* and *III* ( $\rho = 0.82 \text{ cm}^{-1}$  and  $\rho = 0.78 \text{ cm}^{-1}$ , respectively) reported in our previous communications<sup>4,9</sup>.

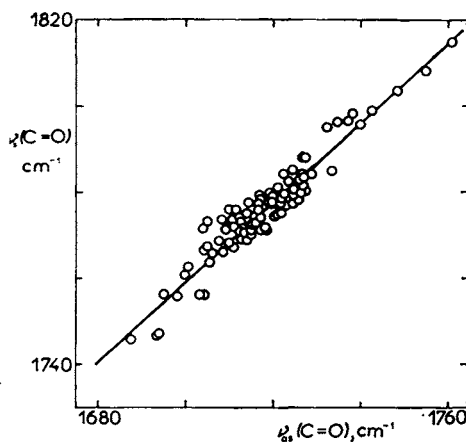
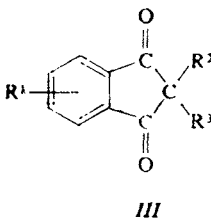
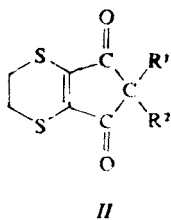


FIG. 1

Relationship between the wavenumbers of symmetric and antisymmetric C=O stretching vibration for maleinimides *I* in  $\text{CCl}_4$  and  $\text{CHCl}_3$

TABLE I  
Wavenumbers of symmetric and antisymmetric C=O stretching vibration (in  $\text{cm}^{-1}$ ) for maleinimides of general formula I

| Compound No | $R^{1a}$                                      | $R^{2a}$                                      | $R^{3a}$ | CCl <sub>4</sub>           |                               | CHCl <sub>3</sub>          |                               |
|-------------|---|---|----------|----------------------------|-------------------------------|----------------------------|-------------------------------|
|             |   |   |          | $\nu_s(\text{C}=\text{O})$ | $\nu_{as}(\text{C}=\text{O})$ | $\nu_s(\text{C}=\text{O})$ | $\nu_{as}(\text{C}=\text{O})$ |
| 1           | PhS   | H   | Ph       | 1774                       | 1720.5                        | 1771.5                     | 1714.5                        |
| 2           | PhNH  | PhS   | Ph       | 1774                       | 1720                          | 1762 <sup>b</sup>          | 1714.5 <sup>b</sup>           |
| 3           | 4-MePh  | Cl  | Ph       | 1784                       | 1727                          | 1785                       | 1724.5                        |
| 4           | H   | H   | Ph       | 1763.5 <sup>b</sup>        | 1723.5 <sup>b</sup>           | 1774.5                     | 1720.5                        |
| 5           | 4-MePh  | PhNH  | Ph       | 1771                       | 1715.5                        | 1768                       | 1710                          |
| 6           | Cl  | Cl  | Ph       | 1799                       | 1742.5                        | 1795.5                     | 1740                          |
| 7           | PhNH  | BuS   | Ph       | 1772.5                     | 1716                          | 1770                       | 1713                          |
| 8           | PhCH <sub>2</sub> S                           | PhNH  | Ph       | 1772.5                     | 1715.5                        | 1769                       | 1713                          |
| 9           | PhNH  | MeS   | Ph       | 1775.5                     | 1716.5                        | 1770                       | 1713.5                        |
| 10          | PhS   | PhS   | Ph       | 1777                       | 1722.5                        | 1774                       | 1717                          |
| 11          | EtOCOC <sup>-</sup> (CN)                      | Ph <sub>3</sub> P <sup>+</sup>                | Ph       | 1756.5                     | 1695                          | 1747                       | 1694                          |
| 12          | C <sub>4</sub> H <sub>8</sub> ON <sup>c</sup> | PhNH  | Ph       | 1768.5                     | 1707.5                        | 1766.5                     | 1704                          |
| 13          | C <sub>4</sub> H <sub>8</sub> ON <sup>c</sup> | Cl  | Ph       | 1775                       | 1722                          | 1771.5                     | 1715.5                        |
| 14          | PhCOC <sup>-</sup> (CN)                       | C <sub>5</sub> H <sub>5</sub> N <sup>+d</sup> | Ph       | 1756                       | 1704.5                        | 1762.5 <sup>b</sup>        | 1699 <sup>b</sup>             |
| 15          | Ph  | NH <sub>2</sub>                               | Ph       | 1775.5                     | 1711.5                        | 1733.5                     | 1705                          |
| 16          | 4-MeOPhNH                                     | NH <sub>2</sub>                               | Ph       | 1775.5                     | 1710                          | 1771.5                     | 1704                          |
| 17          | 4-MePh  | NCS   | Ph       | 1783.5                     | 1727                          | 1783                       | 1726                          |
| 18          | 4-MePh  | SCN   | Ph       | 1781                       | 1727                          | 1780                       | 1725                          |
| 19          | 4-MePh  | (MeO) <sub>2</sub> POS                        | Ph       | 1780.5                     | 1725                          | 1779                       | 1721                          |
| 20          | PhNHCS  | BuNH  | 4-MePh   | 1760.5                     | 1700                          | 1760 <sup>b</sup>          | 1696 <sup>b</sup>             |
| 21          | PhCOCH=CH(E)                                  | BuNH  | 4-MePh   | 1771                       | 1717.5                        | 1769                       | 1714                          |
| 22          | C <sub>2</sub> H <sub>4</sub> N <sup>e</sup>  | H   | 4-MePh   | 1777.5                     | 1722                          | 1775.2                     | 1717                          |

TABLE I  
(Continued)

| Compound No | R <sup>1a</sup>                                  | R <sup>2a</sup>                               | R <sup>3a</sup> | CCl <sub>4</sub>    |                        | CHCl <sub>3</sub>   |                        |
|-------------|--|---|-----------------|---------------------|------------------------|---------------------|------------------------|
|             |  |   |                 | $\nu_s(\text{C=O})$ | $\nu_{as}(\text{C=O})$ | $\nu_s(\text{C=O})$ | $\nu_{as}(\text{C=O})$ |
| 23          | 4-MePhNHCO                                       | 4-MePhNH                                      | 4-MePh          | 1779.5 <sup>b</sup> | 1708 <sup>b</sup>      | 1767                | 1705                   |
| 24          | 4-MePhNH   | H   | 4-MePh          | 1779.5              | 1719.5                 | 1761.5 <sup>b</sup> | 1714.5 <sup>b</sup>    |
| 25          | PhCOCH=CH(E)                                     | 4-MePhNH                                      | 4-MePh          | 1772                | 1717                   | 1720.5              | 1713                   |
| 26          | 4-MePhNH   | MeSCS   | 4-MePh          | 1778                | 1721                   | 1779                | 1717                   |
| 27          | 4-NMe <sub>2</sub> Ph                            | H   | 4-MePh          | 1771.5              | 1718.5                 | 1754 <sup>b</sup>   | 1717.5 <sup>b</sup>    |
| 28          | BuNH   | H   | 4-MePh          | 1771                | 1718.5                 | 1761 <sup>b</sup>   | 1712 <sup>b</sup>      |
| 29          | 4-MePhNH   | 4-MePh  | 4-MePh          | 1769.5              | 1715                   | 1766                | 1708.5                 |
| 30          | 4-ClPhNH   | H   | 4-MePh          | 1775                | 1721                   | 1756 <sup>b</sup>   | 1716.5 <sup>b</sup>    |
| 31          | 4-MeOPhNH  | H   | 4-MePh          | 1780                | 1727.5                 | 1758 <sup>b</sup>   | 1714.5 <sup>b</sup>    |
| 32          | PhNH   | H   | 4-MePh          | 1777.5              | 1719.5                 | 1765 <sup>b</sup>   | 1715.5 <sup>b</sup>    |
| 33          | Me   | Me  | 4-MePh          | 1765 <sup>b</sup>   | 1717 <sup>b</sup>      | 1771.5              | 1711.5                 |
| 34          | H  | H   | 4-MePh          | 1777                | 1724.5                 | 1777.5              | 1720                   |
| 35          | (MeCO) <sub>2</sub> CH                           | PhS   | Me              | 1774                | 1712.5                 | 1773.5              | 1708                   |
| 36          | PhS  | MeNH  | Me              | 1777.5              | 1719.5                 | 1775                | 1714.5                 |
| 37          | (MeCO) <sub>2</sub> CH                           | PhCH <sub>2</sub> NH                          | Me              | 1773                | 1711                   | 1771                | 1708                   |
| 38          | PhCH <sub>2</sub> S                              | MeNH  | Me              | 1774.5              | 1714                   | 1772.5              | 1711                   |
| 39          | (MeCO) <sub>2</sub> CH                           | C <sub>4</sub> H <sub>8</sub> ON <sup>c</sup> | Me              | 1756                | 1703.5                 | 1755.5              | 1698                   |
| 40          | Et <sub>2</sub> NCSS                             | MeNH  | Me              | 1778.5              | 1720                   | 1776.5              | 1716.5                 |
| 41          | C <sub>4</sub> H <sub>8</sub> N—CSS <sup>c</sup> | MeNH  | Me              | 1778.5              | 1720.5                 | 1777                | 1716.5                 |
| 42          | Ph <sub>3</sub> P=C(COOEt)                       | PhS   | Me              | 1763.5              | 1705.5                 | 1762.5              | 1700.5                 |
| 43          | PhCH <sub>2</sub> NH                             | Cl  | Me              | 1767                | 1711                   | 1766                | 1706                   |
| 44          | Ph <sub>3</sub> P=C(COOEt)                       | C <sub>5</sub> H <sub>10</sub> N <sup>f</sup> | Me              | 1746.5              | 1693.5                 | 1745.5              | 1687.5                 |

TABLE I  
 (Continued)

| Compound No | R <sup>1a</sup>   | R <sup>2a</sup> | R <sup>3a</sup>                           | CCl <sub>4</sub>           |                               | CHCl <sub>3</sub>          |                               |
|-------------|---|-----------------|---|----------------------------|-------------------------------|----------------------------|-------------------------------|
|             |   |                 |   | $\nu_s(\text{C}=\text{O})$ | $\nu_{as}(\text{C}=\text{O})$ | $\nu_s(\text{C}=\text{O})$ | $\nu_{as}(\text{C}=\text{O})$ |
| 45          | C <sub>9</sub> H <sub>5</sub> O <sub>2</sub> <sup>g</sup> | Cl              | Me  | 1782.5                     | 1723.5                        | 1781                       | 1721                          |
| 46          | 3,4-Cl <sub>2</sub> PhNH                                  | H               | Me  | 1788                       | 1727.5                        | 1779.5                     | 1722.5                        |
| 47          | CN  | MeO             | H   | 1815                       | 1761                          | 1803.5                     | 1748.5                        |
| 48          | Br  | Br              | H   | 1808                       | 1755                          | 1790 <sup>b</sup>          | 1744 <sup>b</sup>             |
| 49          | Br  | Br              | CH <sub>2</sub> OH                        | 1798                       | 1738                          | 1796.5                     | 1734.5                        |
| 50          | Cl  | Cl              | CH <sub>2</sub> CH=CH <sub>2</sub>        | 1796.5                     | 1737                          | 1795                       | 1732                          |
| 51          | H   | H               | 2,5-Me <sub>2</sub> Ph                    | 1785                       | 1733.5                        | 1784                       | 1728.5                        |
| 52          | H   | H               | CH <sub>2</sub> Ph                        | 1774 <sup>h</sup>          | 1716 <sup>h</sup>             | 1772.5                     | 1712.5                        |
| 53          | H   | H               | 3-COOHPh                                  | 1779                       | 1725                          | 1777                       | 1722                          |
| 54          | H   | H               | 2-MePh                                    | 1779                       | 1725                          | 1778                       | 1718.5                        |
| 55          | H   | H               | 4-ClPh                                    | 1788                       | 1727                          | 1777                       | 1723                          |
| 56          | H   | H               | CH <sub>2</sub> OH                        | 1784                       | 1722.5                        | 1771                       | 1718                          |
| 57          | H   | H               | 6-(2-SMeBT) <sup>i</sup>                  | 1778                       | 1726                          | 1778.5                     | 1722                          |
| 58          | H   | H               | 6-(2-SEtBT) <sup>i</sup>                  | 1780                       | 1726.5                        | 1778                       | 1722                          |
| 59          | H   | H               | 6-(2-SCH=CH <sub>2</sub> BT) <sup>i</sup> | 1779.5                     | 1726.5                        | 1778                       | 1722                          |

<sup>a</sup> The abbreviations used in denoting the substituents R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>: Me methyl, Ph phenyl, Bu butyl, Et ethyl; (E) configuration E with respect to the plane of the C=O bond of substituent. <sup>b</sup> Values excluded from  $\nu_s(\text{C}=\text{O})$  vs  $\nu_{as}(\text{C}=\text{O})$  correlation. <sup>c</sup> Morpholino. <sup>d</sup> 1-Pyridinio. <sup>e</sup> Azididino. <sup>f</sup> Piperidino. <sup>g</sup> 2-(1,3-Indanedionyl). <sup>h</sup> Insoluble. <sup>i</sup> The abbreviation BT means benzothiazolyl.

This means that in maleinimides *I* the influence of the structure upon symmetric and antisymmetric C=O stretching vibrations is more symmetrical than in the case of compounds *II* and *III*. The enlargement of the  $\rho$  value of maleinimides-*I* can be interpreted in the first approach as a decrease of direct conjugation between the C=O groups, resulting from the electron-withdrawing effect of the nitrogen atom in the five-membered imide ring.

*Our thanks are due to Dr E. Sidóová, Institute of Chemistry, Comenius University, Bratislava, for samples of compounds No 57–59. We are also indebted to Mrs. Z. Šusteková and Dr V. Blanáríková, Institute of Chemistry, Comenius University, Bratislava for technical assistance.*

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Translated by the author (A. P.).