

PREPARATION AND PROPERTIES OF PHENYLSUCCINIC ACID DERIVATIVES. IV*. ON THE INFRARED SPECTRA OF SOME SUCCINIMIDES

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Zbadano widma w podczerwieni szeregu imidów i N-alkilimidów pochodnych kwasu fenylobursztynowego. Przeanalizowano charakterystyczny dublet w zakresie drgań rozciągających C=O i stwierdzono, że nie jest on związany z ewentualnym występowaniem międzycząsteczkowych wiązań wodorowych.

Исследованы инфракрасные спектры ряда имидов и N-алкил имидов производных фенилянтранной кислоты. Проанализирован характерный дублет в интервале валентных колебаний C=O и установлено, что он не связан с возможным присутствием интермолекулярных водородных связей.

Infrared spectra were investigated in several imides and N-alkylimides derived from phenylsuccinic acid. The characteristic doublet in the C=O stretching vibration region is discussed and found to be unrelated to the possible existence of intermolecular hydrogen bondings.

Infrared spectra of imides have so far been investigated by numerous authors with particular consideration of maleimide^{1,2)} and succinimide³⁻⁵⁾.

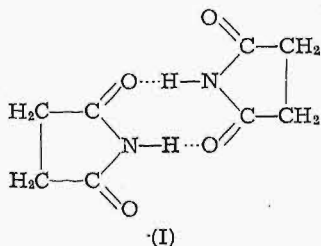
One of the most recent studies concerned with this subject was presented by Uno and Machida⁶⁾, who examined and discussed the infrared spectra of succinimide and maleimide and of their N-deuterated derivatives. They recorded two characteristic absorption bands in the 1700—1772 cm⁻¹ region, that is, in the range of the C=O stretching vibrations. The high-frequency, moderately intense band at 1772 and 1771 cm⁻¹ in succinimide and maleimide, respectively, was assigned by the Japanese authors to stretching vibrations of a free, unbonded carbonyl group; the other, extremely intense band at 1700 cm⁻¹ was attributed to stretching vibrations of a hydrogen-bonded C=O function.

In their assignments, Uno and Machida referred to the structural concept advanced by Mason⁷⁾. Upon examination of the structure of succinimide by the method of X-ray diffraction, Mason suggested the presence of two intermolecular hydrogen bridges. In the light of Mason's experiments, crystalline succinimide may be therefore referred to as a hydrogen-bonded cyclic dimer (I).

To the authors' knowledge, no attempts have been made so far to figure out the energy of such hydrogen bonds, even in a rough and ready way. Nevertheless, it seems beyond doubt that — if hydrogen bonding

* For the preceding paper in this series, see Lange J., Urbański T., Venulet J., *Roczniki Chem.*, 36, 1631 (1962).

does actually exist in cyclic imides — the two C=O groups in succinimide cannot be exactly equivalent to one another and, consequently, may differ more or less in their vibration frequencies. What can be the magnitude of this difference still remains an open question.



On the other hand, a comprehensive survey of the infrared spectra of numerous cyclic compounds with C=O groups, including succinimide and N-methylsuccinimide, was presented by Hall and Zbinden⁸⁾. They recorded two distinct bands attributable to C=O stretching vibrations: at 1771 and 1698 cm^{-1} in succinimide, and 1765 and 1695 cm^{-1} in N-methylsuccinimide. Splitting of the C=O band has been explained by Hall and Zbinden in terms of vibrational interactions of the carbonyl groups. There is every reason to believe that this explanation is properly founded, since an almost identical doublet has been noted by the same authors in three other cyclic N-methylimides as well as in a series of cyclic anhydrides.

Confrontation of the opinions advanced by Uno and Machida⁶⁾ on the one hand, and by Hall and Zbinden⁸⁾ on the other, makes it clear enough that — even if one takes into consideration only the reports published within the last few years — two widely different concepts are advanced to explain the origin of the C=O band splitting in succinimides is due to. It should be positively stressed here that Hall and Zbinden did not engage in any discussion concerned with the possibility of hydrogen bonding in succinimide crystals. They suggested, however, that splitting of the C=O band, as observed in the infrared spectra of succinimides, might be due to a vibrational interaction of the carbonyl groups.

It seems also that the suggestions published by Uno and Machida disregard to a certain extent the ample experimental material made available by infrared spectroscopic examination of N-methylsuccinimide and other N-substituted imides of related structure.

In order to obtain some new data that would make it possible to interpret the C=O band splitting in succinimides in a more consistent and unequivocal way, we have carried out recently an infrared examination of a series of imides and N-alkylimides derived from ring-substituted phenylsuccinic acids⁹⁾.

EXPERIMENTAL

Most of the imides investigated were prepared by pyrolytic decomposition of the corresponding ammonium or amine salts of various *p*-halophenylsuccinic acids as reported earlier⁹⁾. They were purified by recrystallization.

N-Methyl-2,2-dimethylsuccinimide was prepared according to Miller and Long¹⁰⁾ and purified by vacuum distillation.

Commercial samples of succinimide and N-bromosuccinimide were purified by recrystallization.

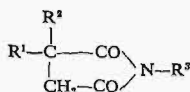
A Hilger H-800 double-beam spectrophotometer with rock salt prisms was used. Except for two N-isohexyl imides (compounds X and XIX) which were molten and analysed neat, all infrared spectra were taken in Nujol mulls.

DISCUSSION

Frequencies of the absorption bands in the C=O stretching vibration region (1530—1800 cm^{-1}) are presented in Tables 1 and 2. In addition, also frequencies of N—H stretching vibrations in N-unsubstituted imides are given.

Table 1

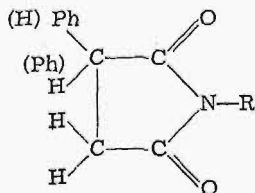
Succinimides



Compd.	R ¹	R ²	R ³	C=O stretching vibration region	N—H stretching vibration region
I	H	H	H	1696 vs, 1773 m	3190, 3080
II	H	H	CH ₃	1658 sh, 1696 vs 1723 sh, 1763 m	—
III	H	H	Br	1580 vw, 1642 sh 1656 sh, 1701 vs 1769 m, 1816 w	—
IV	CH ₃	CH ₃	CH ₃	1651 sh, 1697 vs 1768 m	—

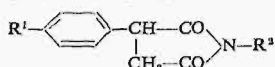
The spectra of compounds (I), (II), and (III) were taken in Nujol mulls. Compound (IV) was analysed neat.

In the discussion, no account is taken of the spectral consequences that may arise from possible conformation differences depending on the positions of the alkyl and aryl substituents. As a matter of fact, there is every reason to believe that isomerism of this type, if any, could hardly be expected to bring about any substantial changes in the infrared curves and, furthermore, to be of great interest to the problem we are concerned with, that is, the problem of C=O stretching vibrations.



A characteristic feature of the infrared spectra of the imides investigated is that they all have several absorption bands in the C=O stretching vibration region (Tables 1 and 2). In most cases, the spectra were taken in crystalline compounds, so that their complexity may be

Table 2

p-Substituted phenylsuccinimides

Compd.	R¹	R²	C=O stretching vibration region	N—H stretching vibration region
V	F	H	1603 s, 1627 m, 1705 vs, 1773 sh, 1815 vw	3129 m, 3057 m
VI	F	C₂H₅	1606 w, 1639 sh, 1695 vs, 1750 sh, 1773 w	—
VII	Cl	H	1702 s, 1785 m, 1750 sh	3159 m, 3067 w
VIII	Cl	CH₃	1597 w, 1696 vs, 1705 vs, 1723 sh, 1773 m	—
IX	Cl	iso-C₆H₁₁	1573 w, 1593 w, 1646 sh, 1691 vs, 1750 sh, 1771 m	—
X	Cl	iso-C₆H₁₃	1597 w, 1660 sh, 1700 vs, 1782 m	—
XI	Br	H	1598 s, 1649 s, 1696 vs, 1750 sh, 1785 m	3175 m, 3071 m
XII	Br	CH₃	1583 w, 1694 vs, 1729 sh, 1754 sh, 1771 m	—
XIII	Br	C₂H₅	1590 w, 1644 sh, 1698 vs, 1770 m	—
XIV	Br	iso-C₆H₁₁	1688 sh, 1696 vs, 1750 sh, 1769 w	—
XV	Br	iso-C₆H₁₃	1595 w, 1682 s, 1710 sh, 1778 w	—
XVI	Br	allyl	1649 sh, 1694 vs, 1750 sh, 1771 m	—
XVII	I	H	1602 s, 1628 s, 1705 vs, 1785 m	3158 s, 4067 m
XVIII	I	CH₃	1694 vs, 1753 sh, 1771 m	—
XIX	I	iso-C₆H₁₃	1588 w, 1703 vs, 1773 m	—
XX	I	allyl	1590 w, 1645 m, 1698 vs, 1771 m	—

Compounds (X) and (XIX) were molten and analysed neat. All other spectra were taken in Nujol mulls.

due to crystal forces. Such an explanation does not sustain, however, confrontation with the results obtained with molten compounds, as was the case with (X) and (XIX) in which the infrared absorption patterns could not reflect the effects of crystal lattices. That the crystalline structure cannot be considered the only factor responsible for the complex shape of the infrared curves in the C=O stretching vibration region is particularly evident from the spectrum of (X).

Although the compounds listed in Table 1 on the one hand and those making up Table 2, on the other, apparently belong to the same structural series, they reveal quite substantial differences as far as their infrared spectra are concerned. Thus, in the case of phenylsuccinimides (Table 2), the aromatic C=C vibration bands may obscure the picture of the C=O stretching vibration bands characteristic of the —CO—NR—CO—system, whereas in the purely aliphatic imides (Table 1) there is no such possibility. On the other hand, the C—C vibrations in *p*-substituted benzenes are known to appear in the infrared spectra approximately at 1600 and 1500 cm⁻¹; the peak appearing near 1600 cm⁻¹ has been recorded in a fairly wide range of 1650—1585 cm⁻¹ depending on the substituent and on the general character of the compound.

In conclusion, it seems legitimate to assume that absorption bands recorded in phenylsuccinimides at frequencies higher than 1650 cm^{-1} should be assigned to the vibrations of carbonyl groups. Two such bands are actually observed in the spectra of the imides we have investigated: a very intense band at $1682\text{--}1705\text{ cm}^{-1}$; and a band of medium or even low intensity at $1769\text{--}1785\text{ cm}^{-1}$. Both bands have been invariably recorded in the spectra of all the compounds under investigation, that is, in N-unsubstituted as well as in N-substituted imides. Moreover, the $\Delta\nu$ value for the two bands is in every case almost the same and seems to be fairly independent of the structure. For example, in succinimide $\Delta\nu$ amounts to 77 cm^{-1} , whereas in N-substituted derivatives of that imide it ranges from 67 to 88 cm^{-1} ; similarly, in N-unsubstituted and N-alkyl phenylsuccinimides, $\Delta\nu$ amounts to $68\text{--}89$ and $68\text{--}96\text{ cm}^{-1}$, respectively.

The experimental results referred to show clearly that the occurrence of at least two absorption bands in the $\text{C}=\text{O}$ stretching vibration region is unrelated to the possible formation of intermolecular hydrogen bonds. The same is true for the frequencies of the two bands and for the $\Delta\nu$ value. Hence, splitting of the $\text{C}=\text{O}$ band into a doublet cannot be explained by the presence of hydrogen bondings, as has been suggested by Uno and Machida⁶. Similarly, one cannot agree with their view that one of these bands represents the vibrations of an unbonded carbonyl group, whereas the other, of a hydrogen-bonded $\text{C}=\text{O}$.

In our belief, the two bands should be assigned to $\text{C}=\text{O}$ stretching vibrations, the splitting observed being due to a vibrational interaction⁸. The doublet has an almost constant $\Delta\nu$ value, which is characteristic of the pyrrole-2,5-dione structure and which undergoes but insignificant changes on substituting the nitrogen atom with various groups.

We would like to emphasize here that our interpretation is by no means intended as a denial of the possible existence of intermolecular hydrogen bonds in succinimides. If the molecules are, however, actually bonded in such a way, the bond forces are low enough to be considered not responsible for splitting of the $\text{C}=\text{O}$ band and unrelated to the magnitude of this effect.

In our investigations, we confined ourselves to the survey of the $700\text{--}3500\text{ cm}^{-1}$ region, so that we could not record the $\text{C}=\text{O}$ deformation vibrations, usually producing infrared absorption bands at appreciably lower frequencies. Similarly, we did not attempt to discuss the rather complex and involved spectral pattern below 1600 cm^{-1} , as we realize that our experimental material does not justify even tentative but reasonably well founded assignments in this region.

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**OTRZYMYWANIE I WŁASNOŚCI POCHODNYCH KWASU
BURSZTYNOWEGO. IV. O WIDMACH W PODCZERWIENI PEWNYCH
IMIDÓW POCHODNYCH KWASU BURSZTYNOWEGO**

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Wśród opublikowanych ostatnio prac poświęconych badaniu i analizowaniu widm w podczerwieni cyklicznych imidów, przede wszystkim pochodnych kwasu maleinowego i bursztynowego, szczegółową interpretację uzyskanych wyników podają Uno i Machida⁶). Dla wyjaśnienia występowania charakterystycznego dubletu w zakresie drgań rozciągających C=O, autorzy ci powołują się na dane Masona⁷), który na podstawie badań rentgenograficznych przypisał krystalicznemu imidowi kwasu bursztynowego budowę cyklicznego dimeru (I) połączonego mostkami wodorowymi. Uno i Machida przyjęli więc, że średniej intensywności pasmo o częstotliwości 1772—1771 cm⁻¹ związane jest z drganiami rozciągającymi wolnej grupy karbonylowej, zaś bardzo intensywne pasmo o częstotliwości 1700 cm⁻¹ wyraża drgania rozciągające grupy C=O związanej mostkiem wodorowym.

Wnioski Uno i Machida nie pokrywają się z danymi, jakie opublikowali wcześniej Hall i Zbinden⁸). Autorzy ci obserwowali występowanie identycznego dubletu w niektórych N-podstawionych imidach oraz w cyklicznych bezwodnikach, a więc w układach wykluczających możliwość tworzenia międzycząsteczkowych wiązań wodorowych.

Dysponując szeregiem związków o podstawowej strukturze imidu kwasu bursztynowego zbadaliśmy ich widma w podczerwieni. Wyniki pomiarów w zakresie drgań rozciągających C=O podane są w tablicach: tablica 1 obejmuje pochodne imidu kwasu bursztynowego, tablica 2 — pochodne imidu kwasu fenylobursztynowego z podstawnikami chlorowcowymi w położeniu *para*. We wszystkich badanych związkach, zarówno zawierających wolną grupę imidową NH — a więc mogących tworzyć wiązania wodorowe — jak i ich N-alkilowych i N-bromowych pochodnych, nie mogących tworzyć takiego wiązania, stwierdziliśmy występowanie charakterystycznego dubletu: średnio intensywnego pasma w granicach 1769—1785 cm⁻¹ oraz bardzo intensywnego pasma w granicach 1682—1705 cm⁻¹. Odległość obu pasm była niemal stała i wynosiła 77 cm⁻¹ w imidzie kwasu bursztynowego, 67—88 cm⁻¹ w jego N-alkilowych pochodnych, 68—89 cm⁻¹ w N-niepodstawionych pochodnych imidu kwasu fenylobursztynowego, oraz 68—96 cm⁻¹ w analogicznych pochodnych podstawionych przy atomie azotu.

Uzyskane wyniki wskazują wyraźnie, że występowanie dubletu w zakresie drgań rozciągających C=O nie jest w żadnym przypadku związane z ewentualną obecnością wiązań wodorowych. Zgodnie z propozycjami Halla i Zbindena wiąże się ono raczej z wzajemnym oddziaływaniem drgań. Wnioski te nie wykluczają w zasadzie możliwości istnienia wiązań wodorowych w badanych imidach.