

CGC-FTIR Characterization of Mononitro and Dinitro Isomers from Nitration Mixtures of Methyl Arylacetates

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Received 29 January 1997

Twenty-one isomeric compounds from nitration of methyl phenyl-, diphenyl-, and (hydroxy)diphenylacetates and the parent compounds were separated by capillary gas chromatography with apolar stationary phase HP-5 and detected by FID and FTIRD. The measured retention indices and infrared spectral data of C=O and NO₂ groups were correlated with molecular structure of analytes. The regularities in GC retention as well as in the FTIR data of isomeric aromatic nitro compounds were formulated. The obtained results can be useful for GC-FTIR identification of ring positional isomers of nitration products of other methyl arylacetates.

Nitration of aromatics is a reaction of both the scientific and practical interest. The mechanisms of the nitration reactions and the search for new reagents with different goals like finding environmentally friendly processes, limiting by-product formation and achieving better selectivity have been unceasingly investigated [1–3]. In this connection the stress is laid upon the problem of detailed analysis of nitration products, mainly of isomeric mononitro and dinitro aromatic compounds.

The identification of the isomeric compounds mainly in complex mixtures usually represents a difficult analytical problem. The hyphenation of capillary gas chromatography (CGC) and Fourier transform infrared (FTIR) detection of separated compounds appears recently to be the most powerful solution. A reliable identification of separated GC peaks to obtain convincing structural information requires a use of selective detectors, which is conclusive in case of infrared spectrometry. The infrared spectra of isomeric compounds are most unique [4]. However, the accurate assignment of all absorption bands is rather complicated. Since the frequencies of the infrared vibrations are sensitive to molecular structural distinctions, the spectra of isomers are different. Due to a good reproducibility of the vapour phase FTIR spectra, even minor differences are rather significant in recognition. In case of the compounds bearing mutually

near polar functional groups the intramolecular interactions can remarkably change the shape of spectra and may be considered as a secondary source of identificational tools [5]. The empirical correlation of infrared C=O stretching vibrational wavenumbers with $\Sigma X^+(R)$ constants of the improved and extended Seth-Paul—van Duyse equation [6, 7] appears to be a further powerful method for the study of structural properties of rather different types of organic compounds. However, infrared spectrometry is particularly poor in distinguishing between homologues without additional relative molecular mass information. The latter can be obtained effectively by mass spectrometry and gas chromatography.

In previous works we solved the problem of the identification of isomers from mononitration and dinitration of both phenyl-, diphenyl- [8], and (hydroxy)diphenylacetic acids [5], as well as their corresponding methyl esters, by programmed temperature capillary gas chromatography with Fourier transform infrared and mass spectrometric detection. In the present study the isothermal GC and FTIR data of the above methyl arylacetates were completed and correlated with the molecular structure. The aim of this generalization is to obtain a suitable tool for identification of ring positional isomers of other nitration products, which is important because of the lack of standard reference materials or their rather difficult

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preparation as well as of deficiency of their GC-FTIR data.

EXPERIMENTAL

Supplies of (hydroxy)diphenylacetic acid were given by Chimica del Friuli, SpA, Torviscosa (Udine, Italy). Separate nitration experiments on phenylacetic, diphenylacetic, and (hydroxy)diphenylacetic acids and their methyl esters, obtained by Fisher methylation, yielding the corresponding mono- and dinitro derivatives, were carried out in a standard fashion. Mixtures of nitrated acids were methylated by the action of diazomethane in diethyl ether. Pure *ortho*-derivatives were obtained by crystallization from a mononitration reaction mixture; the $C_6H_4NO_2$ -*p*, $C_6H_4NO_2$ -*p* derivatives were analogously obtained from a dinitration mixture.

GC-FTIR Measurements

Gas chromatography was performed with a Hewlett—Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) and with an HP Model 5965A IR detector. GC and FTIR data were obtained separately.

GC separation of methyl esters of nitration products was carried out on a fused silica capillary column, 8 m \times 320 μ m i.d., coated with HP-5 as the stationary phase, 0.17 μ m film thickness (Hewlett—Packard, Avondale, PA, USA). The carrier gas was helium at an inlet pressure of 50 kPa and a linear velocity of 44 cm s⁻¹. Samples were diluted with chloroform and volumes of 1 mm³ were injected onto the column with the aid of a splitter operating at a split-

ting ratio of 1 : 50. The injector and FID temperatures were 300°C. The column efficiency was 20,000 effective plates for (hydroxy)bis(*m*-nitrophenyl)acetic acid methyl ester with the retention factor $k = 30$ at 200°C in a GC run with a FID. The retention indices of the nitration products of methyl phenylacetates were measured at 140°C and 160°C, and those of the nitration products of methyl diphenylacetates and (hydroxy)diphenylacetates at temperatures 200°C and 220°C. *n*-Alkanes were added to the mixtures of nitration products in order to determine retention indices at isothermal conditions. Retention indices were measured with an average repeatability of ± 1 index unit.

For obtaining the proper FTIR spectral data the concentrations of injected samples were higher than for GC-FID system but so high only that the baseline separation of investigated isomers was preserved. Spectra were recorded from 4000 to 700 cm⁻¹ at 4 cm⁻¹ resolution and at the scan velocity 1.5 s⁻¹ collected to magnetic disc. The FTIR light-pipe temperature was 310°C. The wavenumbers of absorption bands were determined as average values resulting from three different measurements with a reproducibility of 1 cm⁻¹. Data treatment was carried out with an HP Model 59970C Chemstation, equipped with an HP 9000 Series 300 computer.

RESULTS AND DISCUSSION

Gas Chromatography

The base-line separations of all investigated isomeric mononitro and dinitro derivatives of methyl arylacetates in used capillary column with apo-

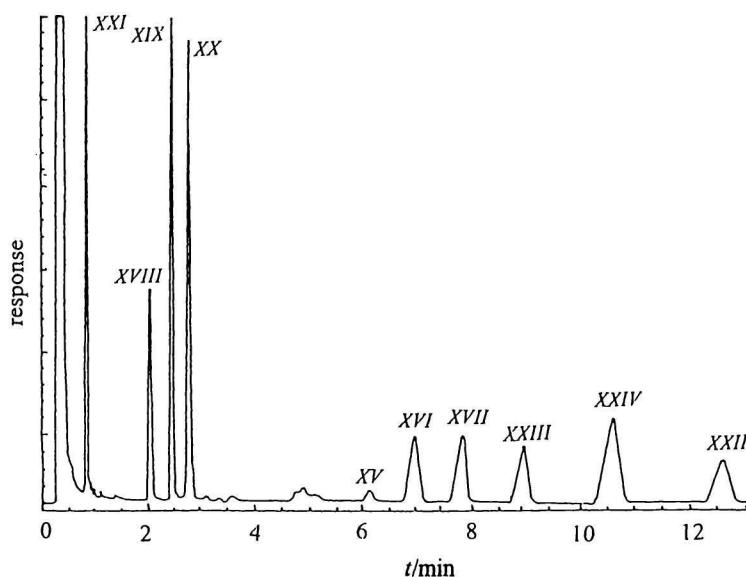


Fig. 1. GC-FID chromatogram of the products from the nitration of methyl (hydroxy)diphenylacetate obtained at 200°C. Peak identification as in Table 4.

Table 1. Retention Indices and their Temperature Coefficients of Methyl Nitrophenylacetates on HP-5 as Stationary Phase

Derivative of the methyl ester of	<i>I</i> (HP-5)	<i>dI/dT</i>
	160 °C	
Acetic acid	1195	0.2
C ₆ H ₄ NO ₂ - <i>o</i>	1554	0.4
C ₆ H ₄ NO ₂ - <i>m</i>	1613	0.4
C ₆ H ₄ NO ₂ - <i>p</i>	1628	0.5
	200 °C	
C ₆ H ₅ , C ₆ H ₅	1775	0.5
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₅	2077	0.7
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₅	2169	0.7
C ₆ H ₄ NO ₂ - <i>p</i> , C ₆ H ₅	2205	0.9
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>o</i>	2418	1.1
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>m</i>	2466	1.0
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>p</i>	2509	1.1
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₄ NO ₂ - <i>m</i>	2583	1.0
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₄ NO ₂ - <i>p</i>	2631	1.1
C ₆ H ₄ NO ₂ - <i>p</i> , C ₆ H ₄ NO ₂ - <i>p</i>	2676	1.2
	200 °C	
Hydroxyacetic acid	1868	0.8
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₅	2183	1.0
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₅	2245	1.0
C ₆ H ₄ NO ₂ - <i>p</i> , C ₆ H ₅	2285	1.1
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>o</i>	2519	1.1
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>m</i>	2558	1.2
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>p</i>	2592	1.2
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₄ NO ₂ - <i>m</i>	2632	1.1
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₄ NO ₂ - <i>p</i>	2677	1.4
C ₆ H ₄ NO ₂ - <i>p</i> , C ₆ H ₄ NO ₂ - <i>p</i>	2732	1.3

lar stationary phase HP-5 at programmed temperature as well as at isothermal conditions were carried out. The chromatograms of individual nitration mixtures obtained at programmed temperature were presented previously [5, 8]. For illustration the chromatogram of nitration mixture of methyl (hydroxy)diphenylacetates at isothermal conditions (200 °C) is given in Fig. 1. The minor peaks detected in the chromatogram were found to be by-products of a different nature.

Since the relationships between the structure and linear retention indices are more complicated than those of logarithmic (Kováts) retention indices [9], the retention indices obtained at isothermal conditions were used for the correlations between structure and retention behaviour as a means of characterization. The Kováts retention indices of methyl esters of isomeric mononitro and dinitro derivatives of (hydroxy)diphenylacetic acid [5] were completed by analogous data measured for similar derivatives of phenylacetic and diphenylacetic acids. The retention indices of investigated nitro derivatives of methyl arylacetates measured by using a capillary column coated with HP-5 as stationary phase *I* (HP-5), as well as their temperature coefficients *dI/dT*, are listed in Table 1.

It follows from the comparison of retention data in the above table that the isomeric methyl esters of mononitro derivatives of all phenylacetic,

diphenylacetic, and (hydroxy)diphenylacetic acids are eluted in the identical order, *i.e.* $I(\text{C}_6\text{H}_4\text{NO}_2\text{-}o) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}m) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)$. In case of isomers of heteronuclearly substituted dinitro derivatives of the methyl esters of both diphenylacetic acid and (hydroxy)diphenylacetic acid the following identical order of elution can be observed: $I(\text{C}_6\text{H}_4\text{NO}_2\text{-}o, \text{C}_6\text{H}_4\text{NO}_2\text{-}o) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}o, \text{C}_6\text{H}_4\text{NO}_2\text{-}m) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}o, \text{C}_6\text{H}_4\text{NO}_2\text{-}p) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}m, \text{C}_6\text{H}_4\text{NO}_2\text{-}m) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}m, \text{C}_6\text{H}_4\text{NO}_2\text{-}p) < I(\text{C}_6\text{H}_4\text{NO}_2\text{-}p, \text{C}_6\text{H}_4\text{NO}_2\text{-}p)$. The sequences found above are analogous to those observed in the case of isomeric methylbiphenyls and heteronuclearly substituted dimethylbiphenyls bearing CH₃ groups in both aromatic rings [10].

The increments of the NO₂ group to the retention indices of aromatic nitro compounds obtained by subtraction of retention index of parent compound from that of corresponding isomer at 200 °C are given in Table 2. It is evident that the increments of the NO₂ group of mononitro and dinitro derivatives increase in the same direction as the retention of corresponding isomers. In the case of mononitro derivatives the above increments are appreciably higher for methyl phenylacetates compared to other nitro derivatives. In both cases (mononitro and dinitro derivatives) the values of retention increments of the NO₂ group for methyl diphenylacetates and (hydroxy)diphenylacetates are

Table 2. Increments of the NO₂ Group to the Retention Index of Methyl Nitrophenylacetates on HP-5 as Stationary Phase at 200 °C

Methyl ester of	$\Delta I(\text{HP-5, 200}^\circ\text{C})/\text{i.u.}$								
	Mononitro derivatives			Dinitro derivatives					
	<i>ortho</i>	<i>meta</i>	<i>para</i>	<i>ortho, ortho</i>	<i>ortho, meta</i>	<i>ortho, para</i>	<i>meta, meta</i>	<i>meta, para</i>	<i>para, para</i>
Phenylacetic acid	364	434	439						
Diphenylacetic acid	299	391	424	635	684	723	798	846	887
(Hydroxy)diphenylacetic acid	315	377	417	651	692	725	764	809	864

Table 3. Increments of the OH Group to the Retention Index of Methyl (Hydroxy)diphenylacetates on HP-5 as Stationary Phase

NO ₂ -Substitution	$\Delta I(\text{HP-5, 200}^\circ\text{C})/\text{i.u.}$
None	93
C ₆ H ₄ NO ₂ - <i>o</i>	106
C ₆ H ₄ NO ₂ - <i>m</i>	76
C ₆ H ₄ NO ₂ - <i>p</i>	80
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>o</i>	101
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>m</i>	94
C ₆ H ₄ NO ₂ - <i>o</i> , C ₆ H ₄ NO ₂ - <i>p</i>	84
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₄ NO ₂ - <i>m</i>	49
C ₆ H ₄ NO ₂ - <i>m</i> , C ₆ H ₄ NO ₂ - <i>p</i>	46
C ₆ H ₄ NO ₂ - <i>p</i> , C ₆ H ₄ NO ₂ - <i>p</i>	56

lower and mutually close. It also follows from the afore-mentioned table that the increments for dinitro derivatives are approximately twice of the values for corresponding mononitro compounds. Using the principle of additivity [10], the values of retention indices of isomeric dinitro derivatives of methyl diphenylacetates calculated from retention increments of NO₂ groups are in average by 21 index units (i.u.) lower than the experimental values. In the case of methyl (hydroxy)diphenylacetates the above difference is only 11 i.u. (it must be noted that the correlated analytes are eluted in the broad range of retention indices 1100 and 2800). For comparison, the average difference between the retention indices for neighbouring eluted isomeric dinitro derivatives of diphenylacetic and (hydroxy)diphenylacetic acids is 47 i.u. (calculated from ten values in the range of 34–74 i.u.), which is approximately two up to four times higher than the average differences between the experimental and calculated values of retention indices.

The increments of the OH group obtained by subtraction of the retention index of a nitro derivative of methyl diphenylacetate from that of corresponding derivative of methyl (hydroxy)diphenylacetate at 200 °C are listed in Table 3. The retention indices of methyl (hydroxy)diphenylacetates are by 46 up to 106 i.u. higher than those of corresponding methyl diphenylacetates. The highest increments of the OH

group are shown by *o*-isomers of both mononitro and dinitro derivatives (84 up to 106 i.u.). In the case of *m*- and *p*-isomers the values of the OH group increments are mutually close, nevertheless they are slightly higher for the *p*-isomers. Generally, the increments of the OH group to the retention index of the methyl (hydroxy)diphenylacetates decrease as the retention of mononitro and dinitro isomers increases (however, some deviation from this rule is observed in the case of *p*-isomers). The above dependence of the retention increments of the OH group exhibits quite an opposite direction compared to analogous dependence of the retention increments of the NO₂ group. It can be explained by the differences in both symmetry and polarizability of molecules of the isomers of these compounds caused by opposite electronic effects, *i.e.* electron-withdrawing and electron-donating effects, of the NO₂ and OH groups, respectively.

From Table 1 it also follows that the dI/dT values for studied class of compounds increase in the following order: parent molecule, mononitro, dinitro derivatives. In case of isomeric mononitro derivatives a little higher dI/dT values were obtained for *p*-isomers when compared with *o*- and *m*-isomers.

Further it is evident from Table 1 that the pairs of methyl esters of bis(*p*-nitrophenyl)acetic acid and (hydroxy)-*m*-nitrophenyl-*p*-nitrophenylacetic acid, *m*-nitrophenyl-*p*-nitrophenylacetic acid and (hydroxy)-bis(*m*-nitrophenyl)acetic acid exhibit at used experimental conditions differences in retention indices which fall within the range of errors of measurements (both cases concern compounds from different nitration mixtures).

Fourier Transform Infrared Spectrometry

The FTIR spectra of nitration products of methyl esters of phenylacetic, diphenylacetic, and (hydroxy)diphenylacetic acids were particularly studied and compared to those of the corresponding parent and model compounds in the region of symmetric and asymmetric stretching vibrations of NO₂ group and stretching vibration of C=O group (see also data in papers [5] and [8]). The typical shape of FTIR spectra of a couple of isomeric nitration products

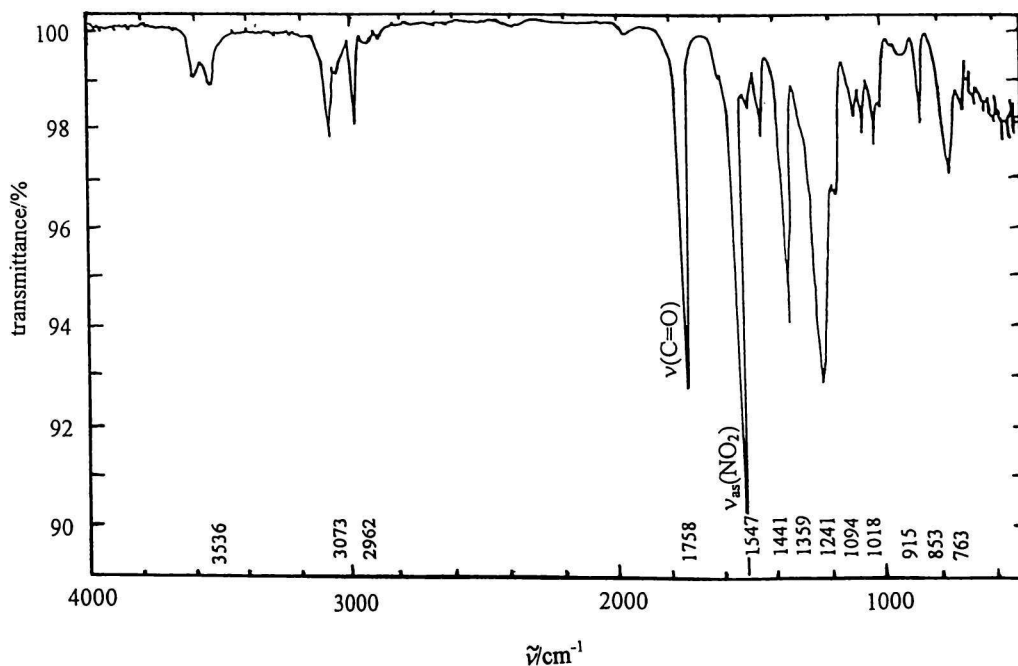


Fig. 2. FTIR spectrum of methyl (hydroxy)-*o*-nitrophenyl(phenyl)acetate.

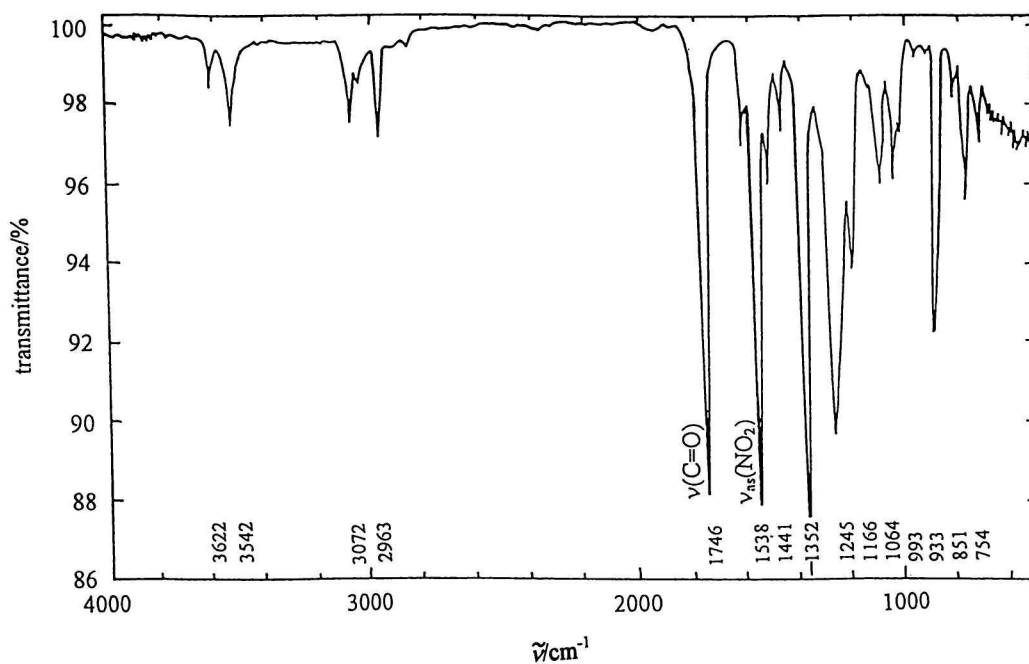


Fig. 3. FTIR spectrum of methyl (hydroxy)-*p*-nitrophenyl(phenyl)acetate.

of methyl (hydroxy)diphenylacetate is illustrated in Figs. 2 and 3. In the above analysis the wavenumbers of the stretching vibration of the hydroxy group and the in-plane deformation vibration of the C—H group of aromatic rings have been also employed. The obtained results can be summarized and generalized as follows.

The mononitro and dinitro derivatives of phenylacetic acid can be easily distinguished on the ba-

sis of the intensity ratio of the C=O stretching and asymmetric NO₂ stretching absorption bands ($\nu(\text{C}=\text{O}) : \nu_{\text{as}}(\text{NO}_2)$). In the case of mononitro compounds the above ratio is lower or equal to 1, while for dinitro derivatives it is always higher than 1.

In the case of hydroxy derivatives of diphenylacetic acid the carbonyl stretching absorption band appeared as the most important tool for the distinction of *o*-nitro derivatives from other positional isomers. In all

Table 4. Wavenumbers of Carbonyl Stretching Vibration and $\Sigma X^+(R)$ Substituent Constants for Methyl Phenyl-, Diphenyl-, and (Hydroxy)diphenylacetates and their Nitration Products

Compound	R ¹	R ²	R ³	$\nu(\text{C=O})/\text{cm}^{-1}$	$\Sigma X^+(R)$
I	H	H	C ₆ H ₅	1759	4.445
II	H	H	C ₆ H ₄ NO ₂ - <i>o</i>	1764	4.484
III	H	H	C ₆ H ₄ NO ₂ - <i>m</i>	1763	4.460
IV	H	H	C ₆ H ₄ NO ₂ - <i>p</i>	1763	4.463
V	H	C ₆ H ₅	C ₆ H ₄ NO ₂ - <i>o</i>	1756	4.352
VI	H	C ₆ H ₅	C ₆ H ₄ NO ₂ - <i>m</i>	1757	4.327
VII	H	C ₆ H ₅	C ₆ H ₄ NO ₂ - <i>p</i>	1757	4.330
VIII	H	C ₆ H ₄ NO ₂ - <i>o</i>	C ₆ H ₄ NO ₂ - <i>o</i>	1757	4.392
IX	H	C ₆ H ₄ NO ₂ - <i>o</i>	C ₆ H ₄ NO ₂ - <i>m</i>	1758	4.367
X	H	C ₆ H ₄ NO ₂ - <i>o</i>	C ₆ H ₄ NO ₂ - <i>p</i>	1758	4.370
XI	H	C ₆ H ₄ NO ₂ - <i>m</i>	C ₆ H ₄ NO ₂ - <i>m</i>	1759	4.360
XII	H	C ₆ H ₄ NO ₂ - <i>m</i>	C ₆ H ₄ NO ₂ - <i>p</i>	1759	4.345
XIII	H	C ₆ H ₄ NO ₂ - <i>p</i>	C ₆ H ₄ NO ₂ - <i>p</i>	1758	4.348
XIV	H	C ₆ H ₅	C ₆ H ₅	1756	4.312
XV	OH	C ₆ H ₄ NO ₂ - <i>o</i>	C ₆ H ₄ NO ₂ - <i>o</i>	1760	4.590
XVI	OH	C ₆ H ₄ NO ₂ - <i>o</i>	C ₆ H ₄ NO ₂ - <i>m</i>	1760	4.565
XVII	OH	C ₆ H ₄ NO ₂ - <i>o</i>	C ₆ H ₄ NO ₂ - <i>p</i>	1759	4.568
XVIII	OH	C ₆ H ₅	C ₆ H ₄ NO ₂ - <i>o</i>	1758	4.550
XIX	OH	C ₆ H ₅	C ₆ H ₄ NO ₂ - <i>m</i>	1747	4.525
XX	OH	C ₆ H ₅	C ₆ H ₄ NO ₂ - <i>p</i>	1746	4.528
XXI	OH	C ₆ H ₅	C ₆ H ₅	1744	4.511
XXII	OH	C ₆ H ₄ NO ₂ - <i>p</i>	C ₆ H ₄ NO ₂ - <i>p</i>	1749	4.546
XXIII	OH	C ₆ H ₄ NO ₂ - <i>m</i>	C ₆ H ₄ NO ₂ - <i>m</i>	1749	4.559
XXIV	OH	C ₆ H ₄ NO ₂ - <i>m</i>	C ₆ H ₄ NO ₂ - <i>p</i>	1749	4.543

m- and *p*-substituted nitro compounds as well as in the unsubstituted parent compound the C=O group is bound with the hydroxy group by intramolecular hydrogen bond [5]. In all derivatives bearing at least one NO₂ group in the *o*-position of benzene rings the C=O group becomes free of intramolecular hydrogen bond as the equilibrium is shifted towards the formation of an intramolecular hydrogen bond between the OH and NO₂ groups [5]. Consequently, all *o*-nitro isomers of hydroxy derivatives of diphenylacetic acid exhibit the location of the C=O stretching vibration by 11–14 cm⁻¹ higher (1760–1758 cm⁻¹) compared to compounds missing the NO₂ group in *o*-position (1749–1744 cm⁻¹).

Another characteristic feature of hydroxy derivatives of diphenylacetic acids bearing NO₂ group in the *o*-position is the shift of the absorption band belonging to the $\nu_s(\text{NO}_2)$ vibration to higher wavenumbers by 7 cm⁻¹ (1359 cm⁻¹), as compared to *p*- and *m*-substituted derivatives (1352 cm⁻¹). This is caused by deconjugation of the NO₂ group with the aromatic ring upon the formation of the afore-mentioned intramolecular hydrogen bond.

For distinction of *m*- and *p*-nitro derivatives of (hydroxy)diphenylacetic acid and for identification of *o*-, *m*-, and *p*-nitro isomers of other phenylacetic and diphenylacetic acid derivatives the wavenumbers of $\nu_{as}(\text{NO}_2)$ vibration can be used. In agreement with the theory of electronic and steric effects of substituents attached to the aromatic ring the $\nu_{as}(\text{NO}_2)$ wavenumbers (1548–1536 cm⁻¹) increase in the order: *p*, *o*, *m*,

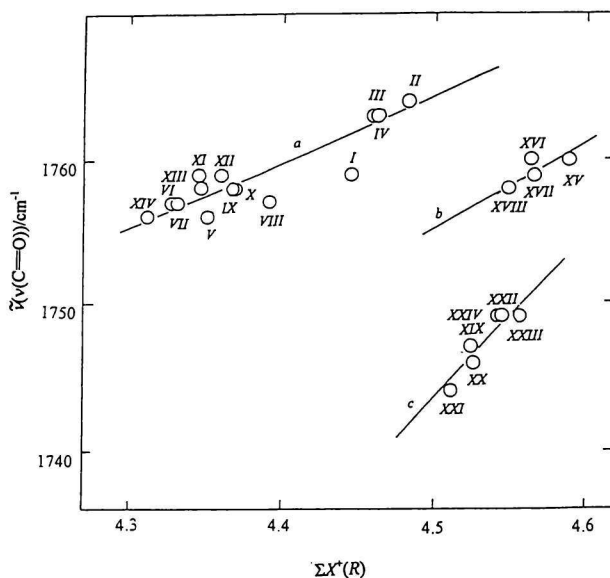


Fig. 4. Dependence of the wavenumbers of carbonyl stretching vibration on $\Sigma X^+(R)$ substituent constants for methyl phenyl-, diphenyl-, and (hydroxy)diphenylacetates and their nitration products. (For *a*, *b*, *c* see the text.)

whereby the differences in the sequence between the isomers are 5–10 cm⁻¹.

In the case of dinitro derivatives the occurrence of two NO₂ groups on the same benzene ring was reliably excluded by analysis of mass spectra [5, 6].

Summarizing the FTIR data obtained for nitration

of phenyl-, diphenyl-, and (hydroxy)diphenylacetic acid methyl esters, the structural types of studied nitro derivatives on the basis of carbonyl stretching vibration wavenumbers of corresponding methyl esters can be compared (Table 4). For this purpose the corresponding $\Sigma X^+(R)$ values, $\Sigma X^+(R) = X^+(R^1R^2R^3C) + X^+(OCH_3)$, in the sense of the improved and extended Seth-Paul—van Duyse equation [6, 7] were calculated. The $\nu(C=O)$ vs. $\Sigma X^+(R)$ correlations (Fig. 4) provide a reasonable splitting of investigated nitro derivatives into three structural types: the methyl arylacetates with a) free carbonyl groups, b) free carbonyl groups in systems where the OH group is bound by intramolecular hydrogen bond to the NO₂ group in the *o*-position of benzene ring, and c) carbonyl groups bound by intramolecular hydrogen bond to OH group.

Acknowledgements. This work was carried out with partial support from funds for inter-university cooperation between Comenius University (Bratislava, Slovakia) and University of Udine (Italy), and also with the support of Italian CNR and MURST funds to A. G. Giumanini.

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