

Note

Reversal of substituent effect on C=O stretching vibrations in hydantoin derivatives: Part II

Gordana S Ušcumlic^{*}, Vera V Krstic['] & Saša Z Dramanic[']

Department of Organic Chemistry
Faculty of Technology & Metallurgy
University of Belgrade Karnegijeva 4,
YU-110001 Belgrade, Yugoslavia

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The IR spectra have been recorded for ten new 3-(*m*- and *p*-substituted benzoyl)-5,5-dimethylhydantoin derivatives **1-10** in the region of fundamental C=O stretching vibrations in dichloromethane, and the frequencies of symmetric and asymmetric νC=O correlated with Hammett substituent constants. When the electron withdrawing substituents are in position-3 of the hydantoin ring., the stretching frequency increases with the increase in the electronegativity. However, the effect of releasing substituents appears to be quite opposite. On the basis of correlations with Yukawa-Tsuno and Swain-Lupton equations, the mechanism of the transmission of substituent effects in hydantoin systems has been discussed.

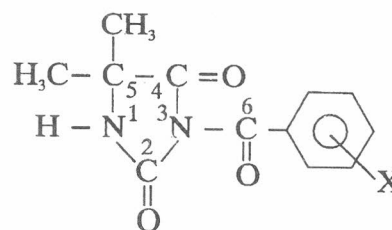
In our previous work we have reported^{1,2} the correlations between the wave numbers of symmetric and asymmetric C=O stretching vibrations of 1,3-disubstituted-5,5-dimethylhydantoin and 3-substituted-5,5-dimethylhydantoin with Taft's inductive σ^{*} substituent constants.

The results have shown that the mechanism of the transmission of substituent effects in hydantoin systems

depends upon the nature of the substituents attached to the nitrogen atom^{1,2}. Similar investigations have been performed with four series of substituted maleinimide derivatives³ and N-substituted-2-phenylacetamides⁴.

In this study the infrared spectra have been recorded for ten 3-(*m*- and *p*-substituted benzoyl)-5,5-dimethylhydantoin derivatives **1-10** in the region of fundamental C=O stretching vibrations in dichloromethane. The wave numbers of symmetric and asymmetric C=O stretching vibrations for the hydantoin derivatives **1-10** have been correlated with Hammett substituent constants⁵ (Table I).

The data given in Table I confirm that the positions of IR frequencies corresponding to the C=O group depend upon the nature of the substituent on the benzene ring. The plots of ν_{as} and ν_s values for (C=O)_{2,4} and (C=O)₆ groups versus σ substituent constants⁵ gave correlations which show deviations from the Hammett equation (Figs 1 and 2). When the electron withdrawing



X	X
1: <i>p</i> -OH	6: H
2: <i>p</i> -OCH ₃	7: <i>m</i> -OCH ₃
3: <i>p</i> -C(CH ₃) ₃	8: <i>p</i> -I
4: <i>p</i> -CH ₃	9: <i>p</i> -Br
5: <i>m</i> -CH ₃	10: <i>p</i> -Cl

Table I — Wave numbers of symmetric and asymmetric C=O stretching vibrations for 3-(*m*- and *p*- substituted benzoyl)-5,5-dimethylhydantoin derivatives **1-10**

Compd	Substituent	ν _s (C=O) _{2,4}	ν _{as} (C=O) _{2,4}	ν _s (C=O) ₆	ν _{as} (C=O) ₆	σ(Ref 5)
1	<i>p</i> -OH	1756.11	1722.56	1582.44	1560.20	-0.37
2	<i>p</i> -OCH ₃	1730.13	1691.24	1577.80	1555.16	-0.27
3	<i>p</i> -C(CH ₃) ₃	1683.54	1654.27	1574.00	1553.20	-0.20
4	<i>p</i> -CH ₃	1686.20	1648.16	1570.24	1550.00	-0.17
5	<i>m</i> -CH ₃	1715.56	1682.16	1566.97	1546.00	-0.07
6	H	1727.00	1691.00	1568.00	1547.40	0.00
7	<i>m</i> -OCH ₃	1751.60	1718.12	1576.00	1549.20	0.12
8	<i>p</i> -I	1760.00	1734.40	1574.20	1550.00	0.18
9	<i>p</i> -Br	1774.43	1746.50	1574.90	1550.60	0.23
10	<i>p</i> -Cl	1784.34	1749.11	1576.60	1552.50	0.23

substituents are on the benzene ring, the stretching frequency increases with the increase in the electronegativity. However, the effect of electron releasing substituents appears to be quite opposite. The electron transfers in the $(C=O)_{2,4}$ groups are more sensitive to the influence of substituents than the $(C=O)_6$ group (Figs. 1 and 2).

To explain these results the frequencies of symmetric and asymmetric C=O stretching vibrations have been correlated with Yukawa-Tsuno equation⁶ and Swain-Lupton equation⁷. These relationships greatly extended the range of applicability of the substituent constants, gave information about the nature of the transition state, and indicated extensive delocalization.

The correlations of the frequencies of C=O stretching vibrations were carried out using multiple linear regression analysis⁸. the results obtained from Yukawa-

Tsuno equation for $\nu_{(C=O)_{2,4}}$ groups gave a fair correlation which can be represented by Eqs 1 and 2, and the poor results for $\nu_{(C=O)_6}$ group (Eqs 3 and 4).

$$\nu_{s(C=O)_{2,4}} = 1720.04 + 186.51\sigma - 151.19(\sigma^+ - \sigma) \quad (R=0.9230, s=14.41) \quad \dots(1)$$

$$\nu_{as(C=O)_{2,4}} = 1685.54 + 202.93\sigma - 157.91(\sigma^+ - \sigma) \quad (R=0.9159, s=16.14) \quad \dots(2)$$

$$\nu_{s(C=O)_6} = 1570.46 + 11.47\sigma - 25.72(\sigma^+ - \sigma) \quad ((R=0.8550, s=2.75) \quad \dots(3)$$

$$\nu_{as(C=O)_6} = 1548.53 - 10.32\sigma - 18.34(\sigma^+ - \sigma) \quad (R=0.8714, s=2.274) \quad \dots(4)$$

The correlations obtained from the data given in **Table I** using Swain-Lupton equation gave satisfactory results which can be represented by Eqs 5, 6, 7 and 8.

$$\nu_{s(C=O)_{2,4}} = 1709.01 + 99.84F - 22.08R \quad (R=0.9418, s=14.35) \quad \dots(5)$$

$$\nu_{as(C=O)_{2,4}} = 1672.39 + 111.65F - 29.70R \quad (R=0.9532, s=14.19) \quad \dots(6)$$

$$\nu_{s(C=O)_6} = 1569.41 + 3.87F - 16.31R \quad (R=0.9325, s=1.91) \quad \dots(7)$$

$$\nu_{as(C=O)_6} = 1548.35 - 0.9230F - 17.54R \quad (R=0.9219, s=1.81) \quad \dots(8)$$

The existence of these correlations has been interpreted as evidence for the significant role of electron-donating effects of the groups X in the transmission of substituent effects. It follows that in 3-(*m*- and *p*-substituted benzoyl)-5,5-dimethyl-hydantoin the mechanism of transmission of substituent effects is governed by competing resonance interactions between the nitrogen atom lone-pair electrons and the carbonyl groups and the substituent attached to the nitrogen atom.

The results thus obtained show that the Swain-Lupton equation is a better model for the description of the transmission of substituent effects in hydantoin systems than the Yukawa-Tsuno equation.

Experimental Section

5,5-Dimethylhydantoin, mp 176-178 °C (Lit.⁹ mp 178-82 °C) has been prepared as reported in literature⁹.

3-Benzoyl-5,5-dimethylhydantoin, mp 120-122 °C, has been prepared by refluxing a mixture of 5,5-dimethylhydantoin and sodium hydroxide in toluene and removing the water formed azeotropically. After cooling, benzoyl chloride was added dropwise with stirring, and the mixture refluxed to effect complete solution. The reaction mixture was cooled, to give 3-benzoyl-5,5-dimethylhydantoin (Lit.¹⁰ mp 121-23 °C).

3-(*p*-Hydroxybenzoyl)-5,5-dimethylhydantoin (mp 62 °C), 3-(*p*-methoxybenzoyl)-5,5-dimethylhydantoin, (mp

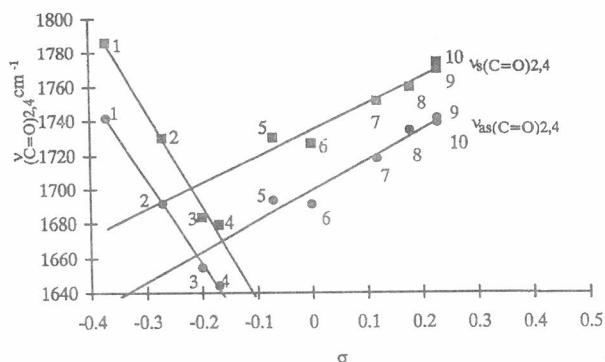


Figure 1—Relationships between the $\nu_{s(C=O)_{2,4}}$ and $\nu_{as(C=O)_{2,4}}$ and σ substituent constants for 3-(*m*- and *p*-substituted benzoyl)-5,5-dimethylhydantoin 1-10.

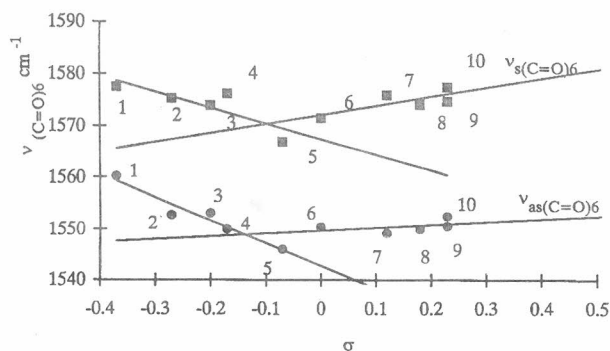


Figure 2—Relationships between the $\nu_{s(C=O)_6}$ and $\nu_{as(C=O)_6}$ and σ substituent constants for 3-(*m*- and *p*-substituted benzoyl)-5,5-dimethylhydantoin 1-10

150 °C), 3-(*p*-*t*-butylbenzoyl)-5,5-dimethylhydantoin (mp 203 °C), 3-(*p*-methylbenzoyl)-5,5-dimethylhydantoin (mp 164 °C), 3-(*p*-chlorobenzoyl)-5,5-dimethylhydantoin (mp 185 °C), 3-(*p*-bromobenzoyl)-5,5-dimethylhydantoin (mp 174 °C), 3-(*p*-iodobenzoyl)-5,5-dimethylhydantoin (mp 155 °C), 3-(*m*-methylbenzoyl)-5,5-dimethylhydantoin (mp 102 °C) and 3-(*m*-methoxybenzoyl)-5,5-dimethylhydantoin (mp 80 °C) were synthesized by the procedure used for preparing 3-benzoyl-5,5-dimethylhydantoin¹⁰.

All the synthesised compounds were identified by elemental analysis, IR and UV data.

The IR spectra were recorded on an FT-IR model BOMEM 100 MB. The wave numbers of asymmetric C=O stretching vibrations were measured in NaCl cells of 1 mm thickness. The less intense absorption bands of symmetric C=O stretching vibrations were obtained by recording the spectra in NaCl cells of 5 mm thickness. The concentration of the solutions met requirements for 70-75% absorption of the examined band maxima. The peak positions were determined by averaging the results of three measurements and are accurate to $\pm 0.5 \text{ cm}^{-1}$.

Acknowledgement

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