SUBSTITUENT EFFECTS IN 1,3-INDANEDIONES*

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The carbonyl stretching frequencies correlate well with substituent constants in a series of 166 1,3-indanediones using improved and extended Seth-Paul–Van Duyse equation. Transmissive factors and group electronegativities have been used to find empirical equations for calculation of substituent constants of more complex structural fragments.

1,3-Indanediones and related cyclic 1,3-diketones were investigated[2−5] to discover linear correlations between the symmetric and asymmetric carbonyl stretching frequencies. In a number of series we have observed[6−11] that the substituents influence significantly the stretching frequencies of 1,3-dicarbonyl system. To evaluate the substituent effects in individual series, we utilized correlations according to Hammett, Brown or Yukawa–Tsuno equations.

Earlier[13] we reinvestigated the original Seth-Paul–Van Duyse equation and derived a simple relationship defining new $X^+(\mathrm{R})$ substituent constants on the basis of electrophilic σ^+ constants:

$$X^+(\mathrm{R}) = 0{\cdot}238\sigma^+ + 1{\cdot}077 . \qquad (1)$$

This improvement and simplification allowed us to apply the $X^+(\mathrm{R})$ substituent constants to a great number of various carbonyl compounds[1,12,13].

The scope of the present work was to scrutinize the extension of validity of the improved Seth-Paul–Van Duyse equation to 1,3-indanedione derivatives.

EXPERIMENTAL

The symmetric (ν_s) and asymmetric (ν_{as}) carbonyl stretching frequencies of compounds *I* and *II* measured prevailingly in our laboratory as dilute solutions in CCl_4 were used for this investigation.

As the majority of data have been already published we assert below just the numbers of compounds and references: Number 1, 2, 6, 13−15, 19, 27−38, 40, 41, 43−50, 52, 60, 62−68, 71, 72, 74, 77, 78, 82−84, 86, 88, 92−97, 99, 100, 103, 104, 108−110, 113, 114, 116, 117, 119−121, 124, 126 and 127 from paper[2]. Number 10, 12, 13, 15, 17, 19 and 20 from paper[10]. Number 2−4

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and 6—8 from paper[9]. Number 2—11 from paper[6]. Number 1 and 3—7 from paper[8]. Number 10—13 and 15—18 from paper[7]. Number 2—4, 6—12, 14, 16—20, 22, 25 and 27 from paper[3]. Number 1—27 from paper[14]. Compound *I*: $Y^1 = Y^2 = H$, $Y^1 = $ furyl from paper[15], Compounds *II*: $Y = H$, $Q = $ 4-isopropylphenyl; $Y = H$, $Q = $ 3-fluorophenyl; $Y = H$, $Q = $ 4-fluorophenyl; $Y = H$, $Q = $ styryl from paper[16].


I

II
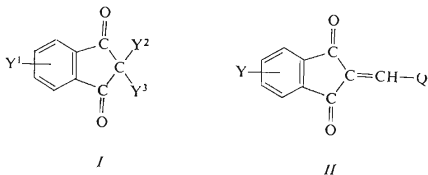
As the CO stretching frequencies of some compounds *II* have not yet been published we bring them in cm^{-1}: for $Y = H$, $Q = $ 1′-methoxyferrocenyl $v_s = 1\ 725$ and $v_{as} = 1\ 684$; for $Y = H$, $Q = $ 1′-ethoxyferrocenyl $v_s = 1\ 726$ and $v_{as} = 1\ 685$; for $Y = H$, $Q = $ 1′-chloroferrocenyl $v_s = 1\ 729$ and $v_{as} = 1\ 689$; for $Y = H$, $Q = $ 2-chloroferrocenyl $v_s = 1\ 730$ and $v_{as} = 1\ 690$; and for (4-ferrocenyl-2-methoxy)phenyl $v_s = 1\ 729\cdot5$ and $v_{us} = 1\ 686\cdot5$.

RESULTS AND DISCUSSION

Substituent Constants

The use of Seth-Paul–Van Duyse equation in the case of 1,3-indanediones required to develop a method of calculation of $X^+(R)$ substituent constants of structural fragments attached to the five-membered cyclic 1,3-dicarbonyl skeleton. For this purpose we dismembered the structure of 1,3-indanediones into two structural fragments R^1 and R^2, whereby the electronic effects of each of one can be expressed by substituent constants $X^+(R^1)$ and $X^+(R^2)$, respectively:
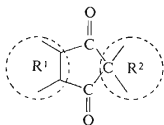
SCHEME 1

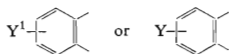According to[17] the substituent constants of groups R^1 and R^2 should be mutually independent and so also additive:

$$X^+(R^1) + X^+(R^2) = \sum X^+(R)$$

In formulas *I* and *II*
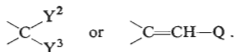
R^1 means

Y^1⊥⟨benzene ring⟩   or Y⊥⟨benzene ring⟩

and

R^2 means

⟩C⟨Y^2 / Y^3 or   ⟩C=CH—Q .

Instead of $X^+(R)$ value of phthaloyl group we employed substituent constant determined for a phenyl group:

$$X^+ \left(\text{⟨benzene ring⟩} \right) \cong X^+(\text{Ph}) = 1 \cdot 07 .$$

The validity of this approximation can be attested by substituting the value of CO stretching frequency measured in CCl_4 for dimethyl phthalate $(1\ 734\ \text{cm}^{-1})$ into the improved Seth-Paul–Van Duyse equation[12]. The $X^+(R)$ value obtained for phthaloyl group $(1 \cdot 07)$ is consistent with $X^+(\text{Ph})$ value.

In the case of 1,3-benz[*f*]indanediones we accepted a similar approximation:

$$X^+ \left(\text{⟨naphthalene ring⟩} \right) = X^+ \left(\text{⟨naphthalene ring⟩} \right)$$

To calculate the $X^+(R)$ substituent constants of more complex structural fragments we employed $X^+(R)$ values of common elemental substituents[12,17].

In the case of 1- and 2-naphthyl groups we determined the values of $X^+(\text{1-Naph}) = 1 \cdot 06$ and $X^+(\text{2-Naph}) = 1 \cdot 04$ using Eq. (*1*) and σ_α^+ constants published previously[18].

For compounds containing a thiocyanate group we have chosen the following way: According to[17]

$$X^+(R) = \delta' + X^+(\text{Me}) \tag{2}$$

and

$$\delta' = 0 \cdot 482 \sigma^*(R) \tag{3}$$

From[19] it is known

$$\sigma^\bullet(R) = 6 \cdot 25 \sigma_1(R) \tag{4}$$

Substituting $X^+(\text{Me}) = 1 \cdot 807$ and using Eqs (*2*) and (*4*) it follows:

$$X^+(R) = 3 \cdot 00286 \sigma_1(R) + 1 \cdot 807 \tag{5}$$

Finally, for $\sigma_I(SCN) = 0.58$ we obtained $X^+(SCN) = 3.55$. The Eq. (5) can be used advantageously to calculate further new $X^+(R)$ constants from σ_I inductive values, which are more available than the original σ^* Taft constants.

To express the electronic effects of a substituted phthaloyl group we utilized Eq. (6) published in[17] and Eq. (1) as well as the results of paper[10].

$$\delta = X^+(R) - X^+(Ph) \qquad (6)$$

From the above mentioned it follows:

$$X^+\left(Y^1\!-\!\!\!\!\underset{\displaystyle}{\bigcirc}\!\!\!\right) = R^+(Ph) + 0.119[\sigma_p^+(Y^1) + \sigma_m^+(Y^1)]$$

The $X^+(R)$ constant of a substituted methylene group can be calculated analogously to the $X^+(R)$ value of a substituted methyl group:

$$X^+\left(>\!\!C\!\!<_{Y^3}^{Y^2}\right) = \chi\left(-\overset{|}{\underset{|}{C}}-\right) + \frac{X^{+2}(Y^2) + X^{+2}(Y^3)}{12X^+(H)} , \qquad (7)$$

where $\chi\left(-\overset{|}{\underset{|}{C}}-\right) = 2.55$ is the electronegativity of an sp^3-hybridized C atom. According to the Eq. (7) the $X^+(R)$ constant of methylene fragment is 2.91.

To determine the $X^+(R)$ value for a methylidene group we have used a similar equation:

$$X^+(=CH_2) = \tfrac{1}{2}\chi(>\!\!C\!=) + \frac{2X^{+2}(H)}{12X^+(H)} = 1.80 , \qquad (8)$$

where $\chi(>\!\!C\!=) = 2.89$ stands for electronegativity of an sp^2-hybridized C atom from the side of single bonds. Using $X^+(=CH_2)$ we calculated according to Eq. (9) the $X^+(R)$ constant for a 1,1-vinylidene group, which is a fundamental skeleton of R^2 in compounds II.

$$X^+(>\!\!C\!=\!CH_2) = \tfrac{1}{2}\chi(=C\!<) + \frac{2X^{+2}(=CH_2)}{12X^+(H)} = 1.32 , \qquad (9)$$

where $\chi(=C\!<) = 2.14$ means the electronegativity of an sp^2-hybridized C atom from the side of double bond. Finally, it can be written for a substituted 1,1-vinylidene fragment:

$$X^+(>\!\!C\!=\!CH\!-\!Q) = X^+(>\!\!C\!=\!CH_2) + \pi'(C\!=\!C)_{s-cis}X^+(Q), \qquad (10)$$

where $\pi'(C{=}C)_{s-cis}$ is the transmissive factor of polar effects for a 1,2-vinylidene group according to definition of Jaffé[20] and determined[13] for an s-cis conformation in respect to the CO group (corresponding to 1,3-indanediones II). If the group Q in compounds II is more complex and consists of a linear chain of subfragments $Q^i (i = 1, 2, 3 \ldots n)$ attached together with single bonds:

$$Q = Q^1 - Q^2 - Q^3 \ldots Q^n ,$$

a general formula can be used to calculate the $X^+(R)$ values of $\mathord{>}C{=}CH{-}Q$ fragments:

$$X^+(\mathord{>}C{=}CH{-}Q) = X^+(\mathord{>}C{=}CH_2) +$$

$$+ \pi'(C{=}C)_{s-cis}[X^+(Q^1) + \gamma(Q^1)(\delta Q^2) + \sum_{i=3}^{n} \delta(Q^i) \prod_{j=1}^{i-1} \gamma(Q^j) \prod_{k=1}^{i-2} \pi'(Q^k)] , \quad (11)$$

π' and γ being transmissive factors of polar effects of subfragments Q^i according to definition of Jaffé[20] and Charton[21], respectively and δ is given by Eq. (6).

A similar approach can be used to determine the substituent constants for more complex structural fragments R^2 of compounds I.

E.g. for $R^2 = \mathord{>}CH{-}Q{-}\langle \rangle{-}Y$
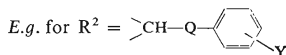
$$X^+(R) = \chi\left(-\overset{|}{\underset{|}{C}}-\right) + \frac{X^{+2}(H) + [R^+(QH) + \gamma(Q)\,\delta_p(Ph) + \pi'(Q)\,\gamma(Q)\,\delta(Y)]^2}{12X^+(H)} .$$

$$(12)$$

The values of transmissive factors used in Eqs $(11)-(12)$ are listed in Table I.

In the case of 1,1'- and 1,3-ferrocenyl groups the transmissive factors γ were not available and therefore we estimated them according to Eqs (13) and (14).

$$\gamma(1,1'\text{-Fc}) = \frac{\pi'(1,1'\text{-Fc})}{\pi'(1,4\text{-Ph})} \quad (13)$$

$$\gamma(1,3\text{-Fc}) = \frac{\pi'(1,3\text{-Fc})}{\pi'(1,4\text{-Ph})} . \quad (14)$$

The above introduced equations, constants and transmissive factors have been used to calculate the $X^+(R^1)$ and $X^+(R^2)$ as well as the $\sum X^+(R)$ values for all 1,3-indanediones I and II.

Correlation Analysis

The arithmetic means of symmetric and asymmetric carbonyl stretching frequencies in a series of 166 1,3-indanediones *I* and *II* provide a statistically significant correlation with $\sum X^+(R)$ values (Fig. 1). The estimates of statistical parameters have been calculated with a significance at $> 95\%$ confidence level using a regression program[25] with a double precision matrix inversion. The correlation analysis renders following results:

$$\bar{\nu} = 33.09\sum X^+(R) + 1\,610.64 \qquad (15)$$
$$\pm 0.70 \qquad\qquad \pm 2.44$$

$r = 0.991$ (correlation coefficient), $s = 2.0$ (standard deviation).

TABLE I
Transmissive factors

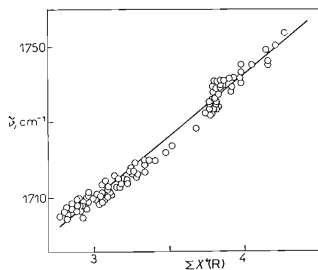| Group	π'	Ref.	γ	Ref.
CH=CH(*s-cis*)	0·766	13	2·23	22
2,5-Furyl(O-O-*trans*)	0·803	1	1·4	23
2,5-Thienyl	0·47	7	1·08	23
1,3-Ferrocenyl	0·38	14	~1·41	this work
1,1'-Ferrocenyl	0·25	14	~0·93	this work
1,4-Phenyl	0·27	24	1·00	[a]
1,4-Naphthyl	0·27	18	1·00	18

[a] By definition.

Fig. 1

Plot of the arithmetical means of ν_s and ν_{as} *vs* $\sum X^+(R)$ values for 1,3-indanediones *I* and *II*

The regression parameters show that the maximal deviation of experimental data from the straight line is 4 cm^{-1} and 61% of points deviate less than 2 cm^{-1}.

The same set of data provides following results of a dual parameter correlation of $\bar{v}$ with substituent constants of structural fragments R^1 and R^2:

$$\bar{v} = 45 \cdot 47 X^+(R^1) + 32 \cdot 94 X^+(R^2) + 1\ 597 \cdot 75$$
$$\pm 10 \cdot 96 \qquad\qquad \pm 0 \cdot 70 \qquad\qquad \pm 11 \cdot 30$$

$r = 0 \cdot 991,\ s = 2 \cdot 0$

The estimate of the first slope is of low statistical significance because of a smaller variation in structure of fragments R^1 comparing to fragments R^2. On the other hand, the estimate of the second slope is statistically more significant and practically equal to the slope of single parameter correlation Eq. (*15*). This is in agreement with our preceding assumption that the electronic effects of structural fragments R^1 and R^2 in 1,3-indanediones should be additive.

It follows that the improved Seth-Paul–Van Duyse equation can be also applied well to the 1,3-indanediones. The present state indicates[26] that this equation is valid for more than eight hundred carbonyl stretching frequencies of organic compounds.

Let us compare Eq. (*15*) with a correlation (Eq. (*16*)) between the symmetric and asymmetric CO stretching frequencies of 1,3-indanediones published earlier[2].

$$v_s = 0 \cdot 781 v_{as} + 412 \cdot 8 \qquad\qquad\qquad (16)$$

$n = 406$ (number of experimental points), $r = 0 \cdot 993,\ s = 1 \cdot 6$

Substituing for $\bar{v} = (v_s + v_{as})/2$ we obtained Eqs (*15*) and (*16*):

$$v_s = 29 \cdot 02 \sum X^+(R) + 1\ 644 \cdot 36 \qquad\qquad (17)$$

$$v_{as} = 37 \cdot 16 \sum X^+(R) + 1\ 576 \cdot 91\ . \qquad\qquad (18)$$

Equations (*17*) and (*18*) can be employed to predict symmetric and asymmetric CO stretching frequencies of a great variety of 1,3-indanediones.

REFERENCES

1. Perjéssy A., Krutošíková A., Olejnik A. F.: Tetrahedron *31*, 2936 (1975).
2. Perjéssy A., Hrnčiar P.: Tetrahedron *27*, 6159 (1971).
3. Perjéssy A., Rotbergs J., Oškāja V. P.: This Journal *41*, 2209 (1976).

4. Perjéssy A., Temkovitz P., Hrnčiar P.: This Journal *41*, 2904 (1976).
5. Perjéssy A., Szemes F., Hrnčiar P.: Acta Fac. Rerum Natur. Univ. Comenianae, Chimia *26*, 73 (1978).
6. Perjéssy A., Hrnčiar P., Krutošíková A.: Tetrahedron *28*, 1025 (1972).
7. Perjéssy A., Hrnčiar P., Frimm R., Fišera Ľ.: Tetrahedron *28*, 3781 (1972).
8. Perjéssy A., Hrnčiar P., Frimm R.: Acta Fac. Rerum Natur. Univ. Comenianae, Chimia *18*, 89 (1973).
9. Krasnec Ľ., Perjéssy A., Hrnčiar P.: This Journal *41*, 2696 (1976).
10. Perjéssy A., Rotbergs J.: Acta Fac. Rerum Natur. Univ. Comenianae, Chimia *27*, 1 (1979).
11. Temkovitz P., Perjéssy A., Hrnčiar P.: Acta Fac. Rerum Natur. Univ. Comenianae, Chimia *27*, 25 (1979).
12. Perjéssy A.: Tetrahedron *29*, 3189 (1973).
13. Perjéssy A.: Tetrahedron *29*, 3207 (1973).
14. Perjéssy A., Toma Š.: Acta Fac. Rerum Natur. Univ. Comenianae, Chimia, in press.
15. Lácová M., Perjéssy A., Hrnčiar P.: Chem. Zvesti *23*, 53 (1969).
16. Agranat I., Lowenstein J., Bergmann E. D.: Israel J. Chem. *7*, 89 (1969).
17. Seth-Paul W. A., Van Duyse A.: Spectrochim. Acta A *28*, 211 (1972).
18. Perjéssy A., Hrnčiar P.: This Journal *37*, 1706 (1972).
19. Palm V. A.: *Osnovi Kolichestvenoi Teorii Organicheskikh Reakci*, p. 31. Khimiia, Leningrad 1967.
20. Jaffé H. H.: Chem. Rev. *53*, 191 (1953).
21. Charton M.: J. Org. Chem. *26*, 735 (1961).
22. Charton M.: J. Org. Chem. *30*, 552 (1965).
23. Exner O., Simon W.: This Journal *29*, 2016 (1964).
24. Zhdanov J. A., Minkin V. I.: *Korelacionii Analiz v Organicheskoi Khimii*, p. 63. Rostov na Donu 1963.
25. Hansch C., Leo A., Elkins D.: J. Chem. Doc. *14*, 57 (1974).
26. Perjéssy A.: Proceedings of IInd Polish-Czech Colloquium on Chemical Thermodynamics and Physical Organic Chemistry, p. 183, Kazimierz 1980.