# 2-BENZYLIDENE[3]FERROCENOPHANE-1,3-DIONES AND THEIR SPECTRAL PROPERTIES

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2-Benzylidene[3]ferrocenophane-1,3-diones were synthesized by condensation of substituted benzaldehydes and [3]ferrocenophane-1,3-dione with triethylamine as catalyst. Benzaldehydes bearing electron-accepting substituents gave bicyclic compounds as by-products; these were formed by extension of the three-membered bridged system to a seven-membered one. A correlation between $\nu(C=O)$ vibrations and $\sigma^+$ constants of substituents was found. The UV and $^1$H-NMR spectra of the prepared compounds are commented.

Condensation of 1,3-indanedione with benzaldehydes afforded, in addition to the corresponding 2-benzylidene derivatives[1,2], also products of autocondensation of indanedione[3]. Addition of 1,3-indanedione to 2-benzylidene-1,3-indanediones led to the corresponding phenylmethylene bis(1,3-indanediones)[4]. Reaction of 5,7(6H)-dibenzo[a,c]cycloheptenedione with substituted benzaldehydes under catalysis of triethylamine in a 1 : 1 ratio gave substituted 6-benzylidene derivatives and at a 1 : 2 ratio substituted phenylmethylene bis(5,7-dioxo-6,7-dihydro-5H-dibenzo-[a,c]cycloheptenes)[5]. This paper is aimed to study the reaction of [3]ferrocenophane-1,3-dione[6] with substituted benzaldehydes and ascertain whether some correlation between the substituent and spectral properties of 2-benzylidene[3]ferrocenophane-1,3-diones was involved.

1'-Cinnamoylferrocenecarboxylic acid was the main product when reacting [3]ferrocenophane-1,3-dione in ethanol (95%) under catalysis of NaOH either at room temperature, or at reflux, *i.e.* an opening of the ring of the starting dione took place[6]. Condensation products having the 3-membered ring maintained were obtained in the excess of the respective aldehyde in a non-aqueous medium using triethylamine as a catalyst (Scheme 1). A longer reaction time and a higher temperature were required. Reactions employing benzaldehydes with electron-donating substituents afforded the condensation product only (Table I), benzaldehydes with electron-accepting substituents furnished the condensation product in a lower yield, whilst the amount of by-product increased.

The structure of substituted 2-benzylidene[3]ferrocenophane-1,3-diones was inferred on the basis of elemental analysis and primarily, on $^1$H-NMR, IR and UV

spectral evidence. Compound $I$ had both cyclopentadienyl rings substituted with the same substituents and consequently, signals of $\alpha$, $\alpha'$ or $\beta$, $\beta^1$ hydrogens in the ${}^1$H-NMR spectra coalesced and therefore two relatively narrow multiplets were observed in this region. Moreover, a multiplet of benzene protons and a notable singlet of the $=CH—C_6H_5$ were seen. All substituted 2-benzylidene derivatives $II—X$ have this singlet maintained. Substituent at the benzene ring is virtually of no effect on its position (Table II). The substituent effect with *para*-substituted derivatives is manifested by the position of resonance signals of 4 protons of the benzene ring. In most cases, these signals were observed as two doublets (AB quadruplet, $J = 9$ Hz).

TABLE I

Analytical Data of Compounds $I—X$

| Compound X | Formula (mol.weight) | Calculated/Found | | | Element % | °C$^a$ (yield) |
|---|---|---|---|---|---|---|
| | | % C | % H | % Fe | | |
| $I$ H | $C_{20}H_{14}FeO_2$ (342·2) | 69·99 69·56 | 4·40 4·08 | 16·27 16·33 | — | 169—171 (66·9) |
| $II$ *p*-Br | $C_{20}H_{13}BrFeO_2$ (421·1) | 57·04 57·08 | 3·11 3·15 | 13·26 13·04 | 18·97$^b$ 19·60 | 180—182 (59·1) |
| $III$ *m*-Br | $C_{20}H_{13}BrFeO_2$ (421·1) | 57·04 57·11 | 3·11 3·17 | 13·26 13·22 | 18·97$^b$ 19·09 | 148—150 (57·9) |
| $IV$ *p*-Cl | $C_{20}H_{13}ClFeO_2$ (376·6) | 63·78 63·53 | 3·47 3·38 | 14·82 14·61 | 9·41$^c$ 9·58 | 180—181 (42·9) |
| $V$ *m*-Cl | $C_{20}H_{13}ClFeO_2$ (376·6) | 63·78 63·74 | 3·47 3·33 | 14·92 14·68 | 9·41$^c$ 9·42 | 165—166 (28·5) |
| $VI$ *p*-CH$_3$ | $C_{21}H_{16}FeO_2$ (356·2) | 70·81 71·07 | 4·52 4·46 | 15·67 15·62 | — | 167—169 (57·1) |
| $VII$ *p*-OCH$_3$ | $C_{21}H_{16}FeO_3$ (372·2) | 67·76 67·89 | 4·33 4·38 | 15·00 15·02 | — | 198—200 (61·4) |
| $VIII$ *p*-N(CH$_3$)$_2$ | $C_{22}H_{19}FeNO_2$ (405·3) | 65·20 66·70 | 4·72 5·08 | 13·78 14·47 | 3·45$^d$ 3·17 | 192, decomp. (20·0) |
| $IX$ *p*-NO$_2$ | $C_{20}H_{13}FeNO_4$ (388·2) | 61·88 62·13 | 3·37 3·28 | 14·38 14·60 | 3·60$^d$ 3·56 | 190—193 (37·9) |
| $X$ *p*-CN | $C_{21}H_{13}FeNO_2$ (351·2) | 71·82 70·98 | 3·73 3·80 | 15·90 15·01 | 3·99$^d$ 3·59 | 192—198, decomp. (42·4) |

$^a$ Crystallized from benzene–light petroleum; $^b$ % Br; $^c$ % Cl; $^d$ % N.

TABLE II
1H-NMR Shifts (δ, ppm) of Compounds I—X

| Compound X | H_α | H_β | o-C_6H_4X | m-C_6H_4X | J_AB Hz | =CH—Ar—X |
|---|---|---|---|---|---|---|
| I   H | 4·538 m, 4 H | 4·708 t, 2 H <br> 4·765 t, 2 H | 7·30—7·045 m, 3 H | 7·55—7·80 m, 2 H | — | 7·875 s, 1 H |
| II   p-Br | 4·548 m, 4 H | 4·738 m, 4 H | 7·516 m, 4 H | | — | 7·825 s, 1 H |
| III   m-Br | 4·538 m, 4 H | 4·725 m, 4 H | 7·0—7·7 m, 4 H | | — | 7·808 s, 1 H |
| IV   p-Cl | 4·563 m, 4 H | 4·750 m, 4 H | 7·318 d, 2 H | 7·608 d, 2 H | 8·7 | 7·835 s, 1 H |
| V   m-Cl | 4·580 m, 4 H | 4·760 m, 4 H | 7·2—7·7 m, 4 H | | — | 7·825 s, 1 H |
| VI   p-CH_3[a] | 4·508 m, 4 H | 4·688 t, 2 H <br> 4·710 t, 2 H | 7·127 d, 2 H | 7·561 d, 2 H | 8·6 | 7·863 s, 1 H |
| VII   p-OCH_3[b] | 4·550 m, 4 H | 4·738 m, 4 H | 6·867 d, 2 H | 7·701 d, 2 H | 8·8 | 7·865 s, 1 H |
| VIII   p-N(CH_3)_2[c] | 4·475 t, 2 H <br> 4·553 t, 2 H | 4·663 t, 2 H <br> 4·740 t, 2 H | 6·610 d, 2 H | 7·710 d, 2 H | 9·1 | 7·863 s, 1 H |
| IX   p-NO_2 | 4·600 m, 4 H | 4·780 m, 4 H | 8·202 d, 2 H | 7·794 d, 2 H | 9·0 | 7·905 s, 1 H |
| X   p-CN | 4·583 m, 4 H | 4·760 m, 4 H | 7·675 m, 4 H | | — | 7·850 s, 1 H |

[a] For p-CH_3 2·313 s, 3 H; [b] for p-OCH_3 3·813 s, 3 H; [c] for N(CH_3)_2 3·025 s, 6 H.

The *p*-CN and *p*-Br derivatives have both these signals coalesced and only a relatively narrow multiplet integrating 4 protons was recorded.
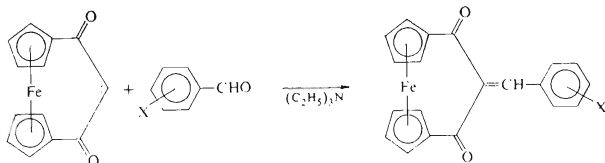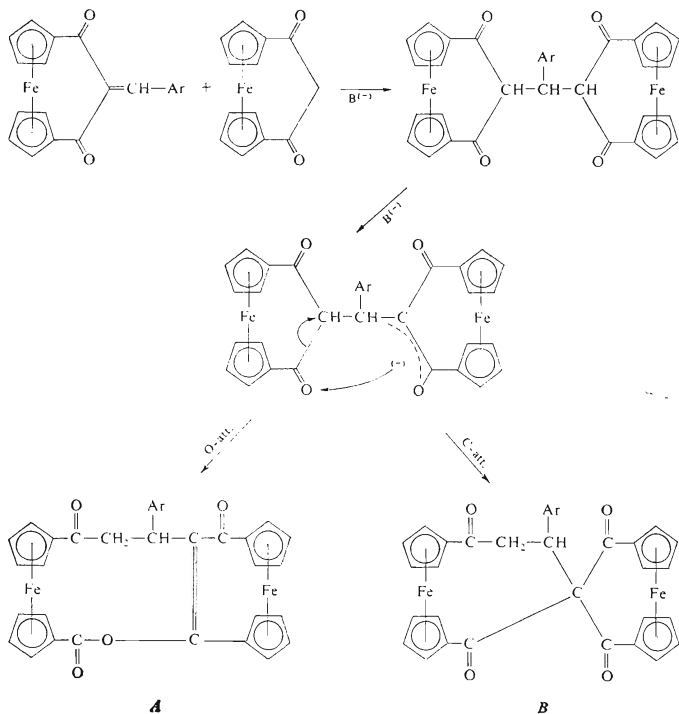


SCHEME 1

2-Benzylidene[3]ferrocenophane-1,3-dione has all carbons in the ring $sp^2$-hybridized. Were the carbonyl groups coplanar with the cyclopentadienyl rings, the tension in the bridge would be great. This tension would be minimalized, if the carbonyl groups were out of the coplanarity with the cyclopentadienyl rings. We suppose, nevertheless, that the cyclopentadienyl ring was in interaction with the =CH—Ar group. UV spectra of the starting dione and its 2-benzylidene derivative differed in that the latter revealed a relatively significant maximum at about 460 nm, belonging to a $d-d^*$ transition of iron electrons. Ferrocene itself displayed this band at 440 nm; it depends on the substituent on the cyclopentadienyl ring[7]. A change in the position of maximum in relation to substituent $(430-475 \text{ nm})$ was seen with substituted 2-benzylidene derivatives; nonetheless, exact reading was impossible due to a very broad band.

All 2-benzylidene derivatives showed a significant maximum in the $300-320$ nm range. We presumed this maximum to belong to a $\pi-\pi^*$ transition of the =CH—Ar group, since the value of extinction coefficient was of a $10^4$ order and the position of maximum shifted only slightly with the change of solvents. Substituents on the benzene ring affected quite substantially the position of maximum. Substituents with an electron-accepting effect shifted the maximum towards lower wavelengths — hypsochromically with regard to the substituted derivative, the electron-donating ones bathochromically. *Para*-Cl and *p*-Br derivatives exerted a strong $+M$ effect, the shift was bathochromic, whereas with *m*-Cl and *m*-Br derivatives the $-I$ effect of halogens came more into account, so that the shift was hypsochromic.

Derivatives of cyclic 1,3-diketones exist in organic solvents prevalently in a keto form, what can be seen in the C=O stretching vibration range of their IR spectra by a double absorption band; the more intense maximum at a lower wave number belonged to an asymmetric vibration and the less intense one at higher wave number to a symmetric vibration of a conjugated 1,3-dicarbonyl system[8-13]. The IR spectra of substituted 2-benzylidene[3]ferrocenophane-1,3-diones and analogous derivatives

of other cyclic 1,3-diketones were in the carbonyl region of the spectrum quite close. Wave numbers of stretching $v_s$ and $v_{as}$ C=O vibration of substituted 2-benzyli-dene[3]ferrocenophane-1,3-diones were the lowest of all known cyclic 1,3-diketones (up to 55 cm$^{-1}$ lower than those of 1,3-indanedione). This is likely caused by a strong electron-donating effect of ferrocene.



SCHEME 2

The $\Delta v = v_s - v_{as}$ values, which can be considered a measure of vibration con-jugation of the 1,3-dicarbonyl system[14], were on an average by 10 cm$^{-1}$ lower than those of analogous 1,3-indanedione derivatives and were the lowest even with further

cyclic 1,3-diketones. It follows that the vibrational coupling of the 1,3-dicarbonyl system was with these ferrocene derivatives very small. Substituted 2-benzylidene[3]-ferrocenophane-1,3-diones $II-X$ had their stretching symmetric and asymmetric

TABLE III
Wave Numbers of Stretching ($\nu$(C=O) Vibrations (cm$^{-1}$) and UV-Maxima of Compounds $I-X$

| Compound | X | $\nu_{as}{}^a$ | $\nu_s{}^a$ | $\Delta\nu$ | Dioxane $\lambda_{max}$, nm | ($\varepsilon \cdot 10^4$) | Methanol$^b$ $\lambda_{max}$, nm |
|----------|---|------|------|------|------|------|------|
| $I$ | H | 1 633 | 1 665 | 32 | 312 | (1·28) | 312 |
| $II$ | $p$-Br | 1 633 | 1 665 | 32 | 320 | (1·37) | 322 |
| $III$ | $m$-Br | 1 635 | 1 666 | 31 | 305 | (1·28) | 304 |
| $IV$ | $p$-Cl | 1 633 | 1 665 | 32 | 318 | (1·63) | 321 |
| $V$ | $m$-Cl | 1 635 | 1 666 | 31 | 304 | (1·27) | 303 |
| $VI$ | $p$-CH$_3$ | 1 631 | 1 662 | 31 | 325 | (1·67) | 330 |
| $VII$ | $p$-OCH$_3$ | 1 628 | 1 656 | 28 | 329 | (1·61) | 335 |
| $VIII$ | $p$-N(CH$_3$)$_2$ | 1 617 | 1 651 | 34 | 427 | (1·64) | 443 |
| $IX$ | $p$-NO$_2$ | 1 636 | 1 668 | 32 | 308 | (1·48) | 305 |
| $X$ | $p$-CN | 1 636 | 1 669 | 33 | 304 | (1·27) | 300 |

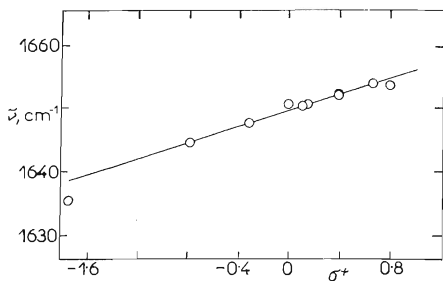$^a$ IR Spectra are measured in chloroform; $^b$ saturated solutions.



FIG. 1
Correlation Between $\tilde{\nu}$(C=O) Vibrations of Substituted 2-Benzylidene[3]ferrocenophane-1,3-diones and $\sigma^+$ Constants of Substituents

vibrations very influenced by substituents at the benzene ring. Electron-donating substituents shifted both $v(C=O)$ vibrations towards lower wave numbers and electron-accepting ones towards higher wave numbers with respect to the unsubstituted derivative.

Hammett correlations between the mean values of wave numbers of symmetric and asymmetric C=O stretching vibration $\tilde{v}$ and $\sigma^+$ constants of substituents[15,17] hold for substituted 2-benzylidene derivatives of 1,3-indanedione, 1,3-benz[f]indanedione, 5,6-dihydro-4,7-dithia-1,3-indanedione and 6-benzylidene-5,7-dibenzo[a,c]-cycloheptanedione. Constants for correlation (Fig. 1) were taken from[17]. For a series of substituted 2-benzylidene[3]ferrocenophane-1,3-diones the relation was found to be $\tilde{v} = 7.43\sigma^+ + 1647.7$; $r = 0.975$. The line slope of this linear correlation ($\varrho = 7.43$ cm$^{-1}$) showed, when compared with those of analogous 2-benzylidene--1,3-indanediones ($\varrho = 8.92$ cm$^{-1}$, ref.[8,10–13]), 2-benzylidene-5,6-dihydro-4,7-di-thia-1,3-indanediones ($\varrho = 5.40$ cm$^{-1}$, ref.[12]), 2-benzylidene-1,3-benz[f]indanediones ($\varrho = 9.72$ cm$^{-1}$, ref.[16]) and 6-benzylidene-5,7-dibenzo[a,c]cycloheptanedione ($\varrho = 4.27$ cm$^{-1}$, ref.[17]), that the sensitivity of the C=O groups towards substituent effects increases in the order: 5,7-dibenzo[a,c]cycloheptanediones < dihydrodithia-indanediones < [3]ferrocenophane-1,3-diones < 1,3-indanediones < 1,3-benz-[f]indanediones.

The reaction of [3]ferrocenophane-1,3-dione with benzaldehydes having electron--withdrawing substituents gave by-products in addition to the corresponding[2]benz-ylidene derivatives. As evidenced by elemental analysis, the by-products were formed of two moles of [3]ferrocenophane-1,3-dione and one mole of a substituted benzal-dehyde. Scheme 2 exemplifies the course of such a reaction.

The $^1$H-NMR spectra of these products showed chemical shifts characteristic of a —CH$_2$—CHAr— grouping of [5]ferrocenophanes[18]. The IR spectra revealed three bands in the $v(C=O)$ vibration range, one of them at 1735 cm$^{-1}$ being ascrib-able to esters. The presence of an ester was backed by the appearance of a $v(C—O—C)$ vibration. Both $^1$H-NMR and IR spectra are in accordance with structure $A$. The decisive proof that the by-product possessed structure $A$ was adduced from the $^{13}$C-NMR spectrum showing chemical shifts of further 7 nonequivalent carbon atoms besides those of benzene and ferrocene rings.

## EXPERIMENTAL

Melting points were determined on a Kofler block. The $^1$H-NMR spectra of 10% CDCl$_3$ solutions were measured at 24°C with a Tesla BS 487 A apparatus operating at 80 MHz, tetramethyl-silane being the internal reference. The chemical shift reading was accurate to $\pm 0.01$ ppm. $^{13}$C--NMR spectra with proton decoupling of saturated CDCl$_3$ solutions were recorded with a JNM--FX 60 apparatus; internal standard was tetramethylsilane. UV spectra of dioxane or methanol solutions were taken with a Perkin–Elmer UV-VIS NIR 450 spectrophotometer at $10^{-4}$M or $10^{-3}$M concentrations. Concentrations of CHCl$_3$ solutions employed for measurement of IR

spectra with a Perkin–Elmer 567 apparatus corresponded to a 75—80% absorption. Silica gel (Kavalier, Votice) was used for column chromatography. [3]Ferrocenophane-1,3-dione was prepared according to[6].

Condensation of [3]Ferrocenophane-1,3-dione with Substituted Benzaldehydes

The respective benzaldehyde (7 mmol) and triethylamine (1·5 ml) were added to [3]ferroceno-phane-1,3-dione (2 mmol) in benzene (40 ml) with stirring. The mixture was heated under reflux for 7 h, the solvent removed under diminished pressure and the residue, washed with benzene, was dissolved in a little amount of benzene and chromatographed (eluent benzene–ethyl acetate 9·5 : 0·5—8·5 : 1·5). Characteristic data of the products are listed in Tables I—III.

When benzaldehydes with electron-withdrawing groups were used, by-products of structure $A$ were obtained in 30—60% yields. Substances with $m$-Cl, $p$-$NO_2$ and $p$-CN only could be characterized.

Product $A$, X = $m$-Cl: a brownred compound, yield 63%, no melting up to 360°C. For $C_{33}H_{23}ClFe_2O_4$ (630·7) calculated: 62·84% C, 3·67% H, 17·71% Fe, 5·62% Cl; found: 61·59% C, 3·58% H, 17·25% Fe, 5·90% Cl. $^1$H-NMR spectrum: $H_B$ 2·84, dd, 1 H; $H_A + H_C + C_5H_4$ 3·75—5·10, m, 18 H; $C_6H_4$ 7·10—7·50, m, 4 H. $^{13}$C-NMR spectrum, CDCl$_3$: $\underline{C}OCH_2$ 198·25; $\underline{C}OC$ 194·68; COO 165·76; $C_6H_5$: $C_1$ 148·95; $C_2$ 126·77; $C_3$ 130·18; $C_4$ 127·18; $C_5$ 134·49; $C_6$ 128·40; $=\underline{C}CO$ 145·87; $-O-\underline{C}=$ 136·19; Fe 85·84, 75·61, 73·90 73·66, 73·33, 73·01, 72·77, 71·71, 70·74, 68·87; CH 45·72; CH$_2$ 42·23. IR spectrum: $\nu$(C—O) 1105, $\nu$(C—O) 1265, $\nu$(C=O) 1625, $\nu$(C=O) 1680, $\nu$(—CO—O) 1735 cm$^{-1}$.

Product $A$, X = $p$-$NO_2$: a brownred compound, yield 38%, no melting up to 360°C. For $C_{33}H_{23}FeNO_6$ (641·3) calculated: 61·81% C, 3·61% H, 17·41% Fe, 2·18% N; found: 61·43% C, 3·46% H, 16·48% Fe, 1·67% N. $^1$H-NMR spectrum: $H_B$ 2·88, dd, 1 H; $H_A + H_C + C_5H_4$ 3·72—5·15, m, 18 H; $C_6H_4$ 7·58, d, 2 H, 8·19, d, 2 H (ABB quadruplet, $J_{AB}$ = 9 Hz).

Product $A$, X = $p$-CN: a brownred compound, yield 32%, no melting up to 360°C. For $C_{34}H_{23}Fe_2NO_4$ (621·3) calculated: 66·49% C, 4·03% H, 17·10% Fe, 2·19% N; found: 65·73% C, 3·75% H, 17·97% Fe, 2·25% N. $^1$H-NMR spectrum: $H_B$ 2·85, dd, 1 H; $H_A + H_C + C_5H_4$ 3·65—5·15 m, 18 H; $C_6H_4$ 7·64 m, 4 H.

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