# Transmission of Polar Effects. Part 17.[1] Ionisation and Esterification with Diazodiphenylmethane of 5-Substituted Triptycene-7-carboxylic Acids and the Alkaline Hydrolysis of their Methyl Esters

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The $pK_a$ values of a series of 5-substituted triptycene-7-carboxylic acids have been measured in 80% (w/w) 2-methoxyethanol–water at 25 °C. The rate coefficients for their esterification with diazodiphenylmethane in 2-methoxyethanol have been measured at 30 °C. The rate coefficients for the alkaline hydrolysis of the corresponding methyl esters have also been determined in 70% (v/v) dioxane–water at both 30.4 and 56.3 °C. In the ionisation reaction reversed substituent polar effects were found and Kirkwood–Westheimer calculations were carried out which confirm that they arise from a field effect. The results for the esterification reaction show similar, but reduced, substituent effects. In the alkaline hydrolysis of the esters a microscopic solvent effect was noted in addition to the dipolar substituent effects.

The triptycene molecule has been previously used as a model system for the study of the transmission of polar effects.[2] In that case the substituents were located at a bridgehead position while the reactive site, a carboxy group, was at the other bridgehead position. Golden and Stock[3] have made a study of transmission of polar effects in 8-substituted 9,10-ethanoanthracene-1-carboxylic acids and 8-substituted 9,10-dihydroanthracene-1-carboxylic acids. They detected a reversal of the normal dipolar substituent effect in such systems. Although the inductive theory of transmission is unable to describe such effects, Golden and Stock[3] used the Kirkwood–Westheimer electrostatic field theory[4] to account for the reversal.

In the present study we have used the triptycene molecule as our 'template'. It has the advantages of high symmetry and rigidity, with no significant interactions between the benzenoid rings. We have studied the reactivity of 5-substituted triptycene-7-carboxylic acids (1) and their corresponding methyl esters in ionisation, esterification with diazodiphenylmethane (DDM), and alkaline hydrolysis.

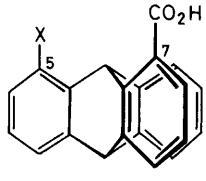
## Results and Discussion

$pK_a$ *Values.*—The $pK_a$ values were measured in 80% (w/w) 2-methoxyethanol–water at 25 °C (Table 1). The $pK_a$ value of the unsubstituted acid (6.88) is as expected from that reported[5] for 2,5-dimethylbenzoic acid (6.92), indicating no 'special' effects associated with the structure of the parent acid. The results in Table 1 indicate that all the dipolar electron-withdrawing and normally acid-strengthening substituents are acid-weakening in this case. The distance between C-5 and C-7 of triptycene is 4.52 Å (see later) and, at this distance, significant steric effects seem unlikely. As with certain systems studied previously,[1,3,6–8] the observed effect must be a consequence of a reversal of the polar effect due to the position of the dipole with regard to the reaction site. The results in Table 1 are closely related to those for the 8-substituted 9,10-ethanoanthracene-1-carboxylic acids.[3] However, the reversal observed for the present acids is, in general, larger than that for the ethanoanthracene system. This might have been expected, as the medium employed by Golden and Stock[2] [50% (w/w) ethanol–water] has a higher dielectric constant (50) than that of 80% (w/w) 2-methoxyethanol–water (39).[9] The observed value of $\log(K_1/4K_2)$ for the dibasic acid, triptycene-2,7-dicarboxylic acid, is 0.53. This is very small in comparison with values for maleic acid, *cis*-cyclopropane-1,2-dicarboxylic acid, and succinic acid, in which intramolecular hydrogen-bonding stabilises the monoanion.[3] The value observed is much closer to those for dibasic acids in which intramolecular hydrogen-bonding is not possible or unlikely. It is somewhat less than for the various 1,8-anthracene systems[3] in 50% (w/w) ethanol–water. Thus intramolecular hydrogen-bonding seems unimportant in the ionisation of triptycene-2,7-dicarboxylic acid.

**Table 1.** $pK_a$ Values of 5-substituted triptycene-7-carboxylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C, and rate coefficients ($k_2$) for esterification with DDM in 2-methoxyethanol at 30 °C[a]

| Substituent | $pK_a$ | $10k_2$/l mol$^{-1}$ min$^{-1}$ |
|---|---|---|
| H | 6.88 | $6.26_5$ |
| Cl | 7.04 | $9.82_5$ |
| CN | 7.03 | $1.87_5$ |
| OMe | 7.16 | $5.82_5$ |
| OH | 7.12 | $5.16_5$ |
| $CO_2Me$ | 7.38 | $7.34_5$ |
| $CO_2H$ | 6.74, 7.04[b] | $4.31_5$, 2.15[b] |
| $CO_2^-$ | 7.99, 7.60[b] | |

[a] The measurements are the mean values of at least two determinations. The $pK_a$ values are reproducible to within ±0.02 unit and the rate coefficients to within ±3%. [b] Statistically corrected value.




(1)

Kirkwood and Westheimer calculations[4] (see Experimental section) have been carried out for polar substituent effects on the acidities of the 5-substituted triptycene-7-carboxylic acids using the two-point charge approximation (Table 2). These are compared with the observed values and, for Cl and CN, can be compared with the results of Golden and Stock[3] for the ethanoanthracenes. The reversal of the polar effect is predicted by the Kirkwood–Westheimer treatment. The agreement between observed and calculated results is generally good except for the $CO_2Me$ substituent. The agreement with Golden and Stock's results[3] is also very good. The reason for the

**Table 2.** Kirkwood–Westheimer calculations for the 5-substituted triptycene-7-carboxylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C

| | | | $\Delta pK_a$ | |
|---|---|---|---|---|
| Substituent | | | Calc.[a] | Found |
| Cl | | | 0.20 | 0.16 |
| CN | | | 0.21 | 0.15 |
| OMe | | | 0.17 | 0.28 |
| OH | | | 0.18 | 0.24 |
| $CO_2Me$ | | | 0.20 | 0.50 |
| | | | $\log(K_1/4K_2)$ | |
| | $\Delta^S$ | $\Delta^C$ | Calc.[b] | Found |
| $CO_2H$ | 1.45 | 3.15 | 4.60 | 0.53 |

[a] By two-point charge approximation. [b] By point dipole approximation.

**Table 3.** Rate coefficients ($k_2$) for the alkaline hydrolysis of methyl 5-substituted triptycene-7-carboxylates in 70% (v/v) dioxane–water[a]

| | $10k_2$/l mol$^{-1}$ min$^{-1}$ | |
|---|---|---|
| Substituent | At 30.4 °C | At 56.3 °C |
| H | 2.66 | 15.9 |
| CN | 3.87 | 27.4 |
| Cl | 1.81 | 10.6 |
| OMe | 2.04 | 10.4 |
| $NH_2$ | 5.87 | 36.4 |
| $O^-$ | 3.78 | $24.1_5$ |
| $CO_2^-$ | 6.15 | 38.3 |
| $CO_2Me$ | 0.740[b] | 5.48[b] |

[a] The measurements are the mean values of at least two determinations. The rate coefficients are reproducible to within ±3%. [b] Statistically corrected value.

disagreement in the size of the reversal for $CO_2Me$ is considered to lie in the considerable uncertainty concerning the dipolar geometry and conformation of this group.

In Table 2 the calculated value of $\log(K_1/4K_2)$ for triptycene-5,7-dicarboxylic acid is given. The parameters $\Delta^S$ and $\Delta^C$ refer to the through-solvent and -cavity contributions. The observed result is much less than that calculated. The calculated result can be considerably reduced by decreasing the embedding factor and/or assuming an extended *trans*-conformation for the $CO_2H$ group. However, the theory appears to work well for diacids in which the carboxy groups are on opposite sides of the molecule.[3] A similar discrepancy was noted by Golden and Stock[3] for 9,10-ethanoanthracene-1,8-dicarboxylic acid. It seems likely that this discrepancy results from a solvent effect. Solvent-sorting may occur with water molecules clustering around the carboxy/alkoxycarbonyl groups and held by hydrogen bonds. This would severely decrease the effective dielectric constant of the medium and thus reduce the effect of the charge, especially if the embedding itself is significantly reduced.

*Esterification with DDM.*—Table 1 shows the rate coefficients for the esterification with DDM of the 5-substituted triptycene-7-carboxylic acids in 2-methoxyethanol at 30 °C. This reaction has been used widely in the study of polar substituent effects.[10] The rate-determining step is the transfer of a proton from the acid to DDM. A plot of the logarithms of the rate coefficients against the $pK_a$ values of the acids gives a scatter with no discernible linear or simple relationship. However, the DDM reaction does appear to be behaving consistently as a probe of reactivity, for this type of behaviour was found previously in the esterification of 8-substituted 1-naphthoic acids[7] and for pseudo-*ortho* and -*gem*-substituted bromo[2.2]paracyclophane-4-carboxylic acids.[6] Thus, the reversals found in the ionisation reaction are either markedly reduced or even revert to a small normal effect in the esterification reaction. It would appear that this arises because the negative end of the substituent dipole can interact significantly with both incipient negative *and* incipient positive charges in the transition state for esterification. In equilibrium ionisation the 'final' state is anionic alone.

**Table 4.** Activation parameters for the alkaline hydrolysis of methyl 5-substituted triptycene-7-carboxylates in 70% (v/v) dioxane–water at 30.4 °C[a]

| Substituent | $\Delta H^‡$/kcal mol$^{-1}$ | $\Delta S^‡$/cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|
| H | 13.1 | −13 |
| CN | 14.4 | −8 |
| Cl | 12.9 | −14 |
| OMe | 11.9 | −18 |
| $NH_2$ | 13.4 | −11 |
| $O^-$ | 13.6 | −11 |
| $CO_2^-$ | 13.4 | −11 |
| $CO_2Me$ | 14.8 | −11 |

[a] Values of $\Delta H^‡$ and $\Delta S^‡$ are considered accurate to within ±300 cal mol$^{-1}$ and ±2 cal mol$^{-1}$ K$^{-1}$, respectively.

*Alkaline Hydrolysis.*—In Table 3 the rate coefficients for the alkaline hydrolysis of the methyl 5-substituted triptycene-7-carboxylates in 70% (v/v) dioxane–water at 30.4 and 56.3 °C are shown. A plot of the logarithms of the rate coefficients against the $pK_a$ values of the corresponding acids shows no discernible linear or simple relationship. Furthermore, the esters with negatively charged substituents react *faster* than the unsubstituted ester. The latter result is quite unexpected on the basis of a polar effect of any kind. There also seems to be no evidence for the occurrence of 'bulk' steric effects retarding hydrolysis for these 'distant' substituents. Severe steric effects of this type are observed for very 'close' substitution in the hydrolysis of methyl 8-substituted 1-naphthoates.[1] A closer examination of the results in Table 3 indicated that for the *dipolar* 5-substituted esters a pattern of reactivity exists. The negative charge in the transition state for alkaline hydrolysis is under the influence of both negative and positive ends of the substituent dipole. Small accelerations or retardations, relative to unsubstituted ester, occur when the effect of the positive or negative end of the dipole predominates, *e.g.* a small retardation for the 5-chloro and small acceleration for the 5-cyano substituent. However, the observed rates for the anionic substituents cannot be related to polar effects alone as the latter would be expected to cause distinct retardations. The transition state for the alkaline hydrolysis of esters is particularly prone to protic solvation effects.[11] It seems likely that protic solvation by water of the anionic sites enables solvation by 'water-bridges' between the anionic substituent and the reaction site in the transition state. This microscopic medium effect would stabilise the transition state and cause the observed rate enhancements. A similar effect has been postulated by Fife and Bruice[12] in a study of the alkaline hydrolysis of cyclopentyl and norbornyl acetates and diol monoacetates. Suitably positioned hydroxy groups appear to assist in providing a microscopic solvent change, *i.e.* by binding and/or orienting solvent molecules, which favours reaction by stabilisation of the transition state. Table 4 shows the activation parameters for the alkaline hydrolysis. The activation entropy

($\Delta S^{\ddagger}$) and enthalpy ($\Delta H^{\ddagger}$) often tend to compensate one another in the control of the rate.

## Experimental

*Materials.*—The 5-substituted triptycene-7-carboxylic acids were prepared mainly by the alkaline hydrolysis of the corresponding esters. These were synthesised by the addition of benzyne to the appropriate anthracenecarboxylic esters. We have used the (non-systematic) numbering scheme for triptycene derivatives employed by Japanese[13,14] rather than American[15,16] workers.

*Methyl 5-Chlorotriptycene-7-carboxylate.*—This was prepared by the method of Sakata *et al.*;[13] m.p. 163—165 °C (from methylcyclohexane) (lit.,[13] 164—165 °C).

*5-Chlorotriptycene-7-carboxylic Acid.*—The foregoing ester (2.4 g, 6.92 mmol), 95% ethanol (100 ml), water (100 ml), and aqueous 10% potassium hydroxide (25 ml) were heated at 75 °C until t.l.c. of a sample showed no ester remaining (*ca.* 2 h). The resulting clear solution was acidified to pH *ca.* 1 with aqueous hydrochloric acid. The ethanol was then removed by distillation at reduced pressure and the solution acidified with concentrated hydrochloric acid before extraction with chloroform. The extract was washed with aqueous sodium chloride solution (saturated), dried ($MgSO_4$), filtered, and evaporated to afford the crude acid (2.3 g, 100%). Recrystallisation from aqueous methanol gave the pure *acid*, m.p. 314—316 °C (Found: C, 75.9; H, 3.9; Cl, 10.5. $C_{21}H_{13}ClO_2$ requires C, 75.8; H, 3.9; Cl, 10.7%).

*Methyl 5-Methoxytriptycene-7-carboxylate.*—This was prepared from methyl 8-methoxyanthracene-1-carboxylate[13] by Friedman and Logullo's method.[15,16] It was crystallised from benzene–petroleum (b.p. 60—80 °C) and then ethyl acetate–petroleum (b.p. 60—80 °C); m.p. 218—220 °C (lit.,[13] 220—221.5 °C).

*5-Methoxy-7-carboxylic Acid.*—This was prepared by the method for the 5-chloro analogue. The *product* (100%) was recrystallised from aqueous acetic acid; m.p. 323—325 °C (lit.,[13] 305—308 °C) (Found: C, 79.9; H, 5.0. $C_{22}H_{16}O_3$ requires C, 79.9; H, 5.2%).

*Methyl 5-Cyanotriptycene-7-carboxylate.*—This was prepared from methyl 8-cyanoanthracene-1-carboxylate by the method of Sakata *et al.*[13] The *ester* was recrystallised from benzene–petroleum (b.p. 60—80 °C); m.p. 279—280 °C (Found: C, 82.0; H, 4.4$_5$; N, 4.1$_5$. $C_{23}H_{15}NO_2$ requires C, 81.9; H, 4.4; N, 3.9%).

*5-Cyanotriptycene-7-carboxylic Acid.*—The foregoing ester (0.9 g, 2.67 mmol) was dissolved in ethanol. Water (35 ml) and aqueous 10% potassium hydroxide (7 ml) were added, and the mixture was stirred for 55 min at 70 °C. The clear solution was cooled to 0 °C and diluted with water (90 ml). Aqueous 5% hydrochloric acid was added until the pH reached 6. The ethanol was then evaporated off and the aqueous residue was acidified with concentrated hydrochloric acid to afford a colourless precipitate. The *solid* was filtered off, dried, and recrystallised from methanol (yield 0.7 g, 81%); m.p. 313—315 °C (Found: C, 81.2; H, 4.4; N, 4.9. $C_{22}H_{13}NO_2$ requires C, 81.7; H, 4.0; N, 4.3%).

*5-Aminotriptycene-7-carboxylic Acid.*—The foregoing 5-cyano derivative (2.3 g, 7.1 mmol) and thionyl chloride (5.8 ml) were refluxed in tetrahydrofuran (11 ml) for 2 h; the volatile material was then removed to give the crude acid chloride. This was dissolved in tetrahydrofuran (40 ml) and cooled to 0 °C. Sodium azide (0.6 g, 25 mmol) in water (12 ml) was then added with stirring. After stirring for 3 h at 0 °C, the mixture was diluted with water; the precipitated azide was filtered off, dried (2.3 g, 93%), and added to boiling benzene (100 ml) in small quantities. The mixture was refluxed for 3 h. Evaporation afforded the crude isocyanate 2.2 g, 100%). The isocyanate, ethanol (86 ml), potassium hydroxide (11.8 g), and water (30 ml) were refluxed for 16 h. The mixture was cooled and neutralised with hydrochloric acid to pH 6. Then acetic acid was added to precipitate a colourless solid. The mixture was extracted with ethyl acetate and the extract was dried ($MgSO_4$) and evaporated to afford the crude amino acid (1.5 g, 69%).

*Methyl 5-Aminotriptycene-7-carboxylate.*—The foregoing amino acid (0.4 g, 1.2 mmol), methanol (10 ml), and concentrated sulphuric acid (1 ml) were refluxed for 3 h. After cooling, the mixture was diluted with benzene and then washed twice with water. The benzene solution was then dried ($MgSO_4$) and evaporated to afford the crude ester (0.3 g, 92%). Recrystallisation from methanol gave the *ester*, m.p. 207—208 °C (Found: C, 80.4, H, 5.0; N, 4.1. $C_{22}H_{17}NO_2$ requires C, 80.7; H, 5.2; N, 4.3%).

*Methyl Triptycene-5-carboxylate.*—This *ester* was prepared from methyl anthracene-1-carboxylate by the method of Sakata *et al.*,[13] m.p. 204—205 °C (from methylcyclohexane) (Found: C, 84.4; H, 5.2. $C_{22}H_{16}O_2$ requires C, 84.6; H, 5.16%).

*Triptycene-5-carboxylic Acid.*—This was prepared by the method for the 5-chloro-7-carboxylate acid. The *product* (90%) was recrystallised from aqueous dioxane, then from ethanol; m.p. 265—270 °C (Found: C, 84.2; H, 4.8. $C_{21}H_{14}O_2$ requires C, 84.5; H, 4.6%).

*Dimethyl Triptycene-5,7-dicarboxylate.*—This was prepared from dimethyl anthracene-1,8-dicarboxylate by the method of Kuritani *et al.*[14] It was recrystallised twice from methanol, then from benzene–petroleum (b.p. 40—60 °C); m.p. 175—176 °C (lit.,[14] 176—177 °C).

*Triptycene-5,7-dicarboxylic Acid.*—This was prepared by the method for 5-chlorotriptycene-7-carboxylic acid. The *acid* was recrystallised twice from 2-methoxyethanol; had m.p. > 360 °C. The neutralisation equivalent was 338.5 (theory 342) (Found: C, 76.5; H, 4.3. $C_{22}H_{14}O_4$ requires C, 77.2; H, 4.1%).

*5-Methoxycarbonyltriptycene-7-carboxylic Acid.*—Triptycene-5,7-dicarboxylic acid (0.846 g, 2.4 mmol) was stirred with sodium methoxide (0.129 g, 2.4 mmol) in methanol for 1 h under reflux. The solvent was removed under reduced pressure and the product was then dissolved in the minimum of 2-methoxyethanol. A solution of diazomethane in ether was added until a green colour persisted. The mixture was evaporated and the residue was treated with aqueous hydrochloric acid and extracted with ethyl acetate. The extract was washed with aqueous sodium chloride (saturated), dried ($MgSO_4$), and evaporated. The residue was dissolved in hot methanol and the solution filtered. Evaporation left a mixture of mono- and di-ester (0.6 g). The mixture was dissolved in methanol and aqueous 5% sodium hydroxide (1 ml) was added. Water (3 ml) was added to precipitate the diester, which was filtered off. The filtrate was acidified with aqueous hydrochloric acid and extracted with benzene. The benzene solution was dried ($MgSO_4$), filtered, and then evaporated. The *mono ester* was recrystallised from methanol–benzene; m.p. 323—325 °C (Found: C, 77.3; H, 4.4. $C_{23}H_{16}O_4$ requires C, 78.2; H, 4.5%).

*5-Hydroxytriptycene-7-carboxylic Acid.*—5-Methoxytriptycene-7-carboxylic acid (0.440 g, 1.3 mmol) was dissolved in boiling acetic acid (10 ml) and hydroiodic acid (10 ml) was added. After refluxing for 10 h, the solution was cooled to about 10 °C, diluted with water (10 ml) and extracted several times with ether. The extract was washed with aqueous 10% sodium hydrogen sulphite, then with aqueous sodium chloride (saturated), and dried ($MgSO_4$). Evaporation left the product as a *hydrate*. The latter was recrystallised from aqueous acetic acid, then from aqueous ethanol; m.p. 294—295 °C (Found: C, 75.9; H, 4.2. $C_{21}H_{14}O_3 \cdot H_2O$ requires C, 75.9; H, 4.2%). The neutralisation equivalent was 340 (theory for hydrate, 332).

*Methyl 5-Hydroxytriptycene-7-carboxylate.*—5-Hydroxytriptycene-7-carboxylic acid was treated as for the 5-amino ester. The *product* (99%) was recrystallised from aqueous ethanol; m.p. 255—256 °C (Found: C, 80.7; H, 5.1. $C_{22}H_{16}O_3$ requires C, 81.0; H, 4.9%).

*General.*—All products had i.r., $^1H$ n.m.r., and mass spectra in accord with the stated structures. The solvents and DDM were prepared as previously described.[17,18]

*Measurements.*—The $pK_a$ values and the rate coefficients for esterification with DDM were determined as described previously.[17,19] The rate coefficients for the alkaline hydrolysis of the esters were measured as previously described.[20] The substrate and hydroxide anion concentrations were $2.5 \times 10^{-4}$ and $5 \times 10^{-3}$ to $1 \times 10^{-1}$M, respectively. The reactions were followed at the $\lambda$ value showing maximum difference between substrate and product, *i.e.* 300—350 nm. The reactions were first-order in both substrate and hydroxide. The latter observation was established with particular care for the 5-hydroxy and -carboxy esters, both being anionic in an excess of base. As the reactions were carried out in an excess of base, the resulting first-order behaviour could be observed without deviation for three 'half-lives'. The products (the anions of the corresponding acids) were obtained quantitatively from preparative-scale reactions and their identities were confirmed by spectral comparison with the acids in basic solution. However, for dimethyl triptycene-5,7-dicarboxylate, a consecutive reaction is observed as first one and then the other ester group is hydrolysed. An initial rate method due to Hall *et al.*[21] was used to obtain the rate coefficient for the first hydrolysis. The monoester was treated as already described to obtain the second rate coefficient.

*Kirkland and Westheimer Calculations.*—These were carried out in a similar way to that described previously[6] for a spherical, two-point charge model.[4] The structural parameters used were obtained from an *X*-ray crystallographic study of 1-bromotriptycene.[22] The cavity has a radius of 5.9 Å and is located 0.6 Å away from the midpoint of the line defined by C-1 and C-6 towards C-6. The dipole moments of the relevant substituents are taken to be those of the similarly substituted benzenes.[23] Those of the substituents OMe, OH, and $CO_2Me$ are considered to be on the line joining the substituent to the aromatic ring (assuming free rotation). The same assumptions regarding embedding and placement of the acidic proton were made as in our previous study.[6] The same problem as was indicated before[1] arises from the positioning of the positive end of the dipoles. It is however less critical in this study and, for all substituents, the position is taken as that for chloro substituent, *i.e.* C-5. The value of log $(K_1/4K_2)$ was calculated by using the point charge approximation of Kirkwood and Westheimer.[4]

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