mixture of 286 mg of 4,5-diphenyl-1,3-dithiole-2-thione (**6**), 0.5 mL of trimethyl phosphite, and 10 mL of toluene was heated under reflux under nitrogen for 24 h. The red solution was evaporated and the residue was recrystallized from acetonitrile to give 54 mg (21%) of orange crystals, mp 261.5–263 °C (lit. 262–263 °C).[3b] Spectral data were identical with authentic sample.

$\Delta^{2,2'}$-Bis(4,5-dicarbamide-1,3-dithiolidene) (7). A mixture of 76 mg of finely ground **1** and 10 mL of concentrated hydrochloric acid was allowed to stand for 2 weeks at room temperature under stirring. The solid was filtered and washed with water and with ethanol. After drying 74 mg (79%) of purple solids was obtained: mp > 360 °C; IR (KBr) 3600–2900, 1670, 1390–70 cm^{-1}; UV (DMF) λ_{max} 449 nm (log ϵ 3.31), 319 (4.18); *m/e* 376. Anal. Calcd for $C_{10}H_8N_4O_4S_4$: C, 31.90; H, 2.14; N, 14.88; O, 17.00. Found: C, 31.67; H, 2.29; N, 14.57; O, 17.10.

$\Delta^{2,2'}$-Bis(4,5-dicarboxy-1,3-dithiolidene) (8). A mixture of 0.637 g of **3**, 1.0 g of potassium hydroxide, and 40 mL of ethanol was heated under reflux for 1 h. The resulting orange potassium salts were filtered and dissolved in 15 mL of water. Neutralization with hydrochloric acid yielded purple solids. These were filtered and dried without washing, because of water solubility. Recrystallization from DMF–ether gave 0.590 g (100%) of light purple crystals: mp > 360 °C; IR (KBr) 3600–2700, 1550, 1503, 1360 cm^{-1}; UV (DMF) λ_{max} 477 nm (log ϵ 3.33), 311 (4.17), 302 (4.10). Anal. Calcd for $C_{10}H_4O_8S_4$: C, 39.25; H, 9.41; O, 29.88. Found: C, 39.21; H, 9.56; O, 29.97.

$\Delta^{2,2'}$-Bis(4(5)-carboxy-1,3-dithiolidene) (9). A. 8 (63 mg) was suspended in 5 mL of acetic anhydride and heated under reflux for 0.5 h. Red crystals precipitated and were filtered and dried to give 36 mg (76%) of **9:** mp > 360 °C; IR (KBr) 3400–3200, 1650, 1540, 1425, 1295 cm^{-1}; ^{13}C NMR (DMSO-d_6) δ from TMS 160.0 ($C^*{=}O$), 132.6 ($=C^*CO$), 128.7 ($=C^*H$), 110.1 ($S_2C{=}CS_2$). Anal. Calcd for $C_8H_4O_4S_4$: C, 32.86; H, 1.38; O, 21.89. Found: C, 32.84; H, 1.49; O, 22.08.

B. A mixture of 0.400 g of **3**, 18 mL of water, 18 mL of concentrated hydrochloric acid, and 50 mL of glacial acetic acid was heated under reflux for 3 h. The resulting solids were filtered and dried and yielded 0.250 g (92%) of red crystals **9**.

$\Delta^{2,2'}$-Bis(4,5-dicarboxy anhydride-1,3-dithiolidene) (10). A mixture of 60 mg of **8**, 0.5 mL of thionyl chloride, and 3 mL of methylene chloride was heated under reflux for 1 h. The dark solution was evaporated to give the dark residue, which was crystallized from *n*-hexane to give 53 mg (100%) of **10** as dark brown needles: mp > 360 °C; IR (KBr) 1850, 1780, 1560, 1255 cm^{-1}; *m/e* 344.

Anal. Calcd for $C_{10}O_6S_4$: C, 34.88; O, 27.88. Found: C, 35.01; O, 27.92.

Tetrathiafulvalene, $\Delta^{2,2'}$-Bis(1,3-dithiolidene). A mixture of 141 mg of **9** and 4 mL of pyridine was sealed in a heavy wall glass tube under argon. The tube was heated at 250 °C for 1.5 h. After cooling, the solvent was evaporated. The dark residue was extracted with three 10-mL portions of acetonitrile. The extracts were evaporated and the residue was sublimed at 110 °C (0.3 mmHg) to give 63 mg of orange product (63%). The structure was identified by the ^{1}H NMR spectra.

Registry No.—**1**, 55052-32-9; **2**, 1005-10-3; **3**, 26314-39-6; **4**, 7396-41-0; **5**, 23780-79-2; **6**, 17534-37-1; **7**, 64414-04-6; **8**, 59269-79-3; **9**, 51751-19-0; **10**, 64414-03-5; **11**, 64414-02-4; **12**, 55513-26-3; triphenylphosphine, 603-35-0; trimethyl phosphite, 121-45-9; triphenyl phosphite, 101-02-0; TTF, 31366-25-3.

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Carbon Acidity. 55. Acidity of 8,8-Dimethyl-8,12b-dihydrobenz[*a*]fluoranthene. Conjugating Effect of a Coplanar Phenyl[1]

Andrew Streitwieser, Jr.,* and Linda L. Nebenzahl

Department of Chemistry, University of California, Berkeley, California 94720

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The preparation of the title compound (DDF) is described. Its anion is of the 9-phenylfluorenyl type with the phenyl group constrained to coplanarity with the fluorenyl moiety by the *gem*-dimethyl bridge. The pK_{CsCHA} of DDF, 15.45, is 3.0 p*K* units more acidic than 9-phenylfluorene. Of the total ΔpK_{CsCHA} of 7.6 units from fluorene itself, about one-third is attributed to polar effects and two-thirds to conjugation.

The phenyl group in 9-phenylfluorenyl anion (PF^-) is known to conjugate only weakly with the fluorene nucleus, undoubtedly because interactions with the 1- and 8-fluorene hydrogens prevent coplanarity. 9-Fluorene substitutents that exert inductive effects only have been shown to give a linear correlation in a plot of the relative acidity (pK_{CsCHA}) in the cesium cyclohexylamide (CsCHA) system against the polar substituent constant σ^*.[2] According to this correlation, the phenyl substituent with $\sigma^* = 0.600$[3] would provide a pK_{CsCHA} of 19.5 for a 9-phenylfluorene (PF) in which the phenyl group exerted a polar effect only.

In an important recent paper, Bordwell and McCollum[4]

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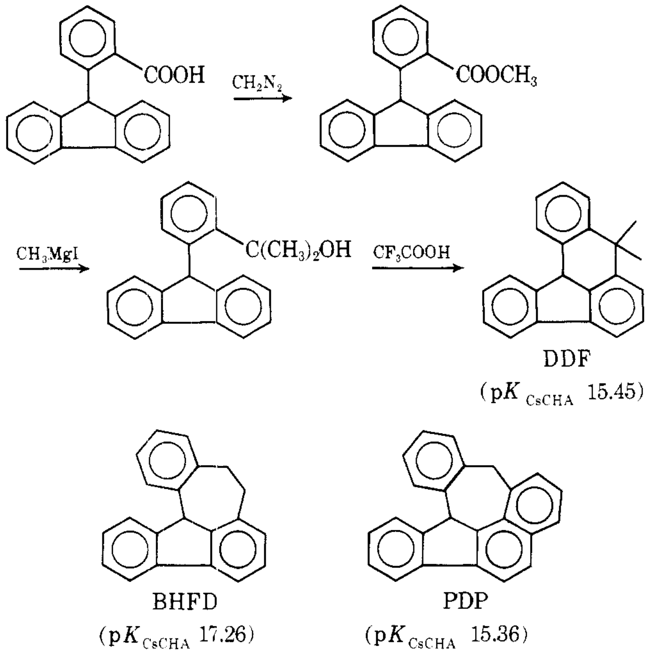
Chart I



DDF
(pK_{CsCHA} 15.45)

BHFD
(pK_{CsCHA} 17.26)

PDP
(pK_{CsCHA} 15.36)

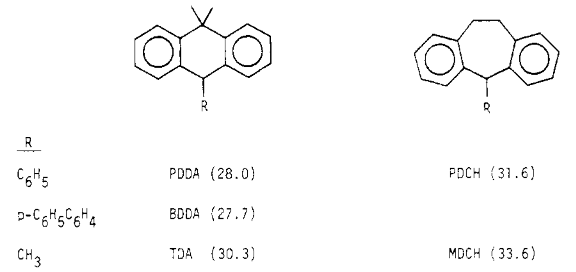


Figure 1. pK_{CsCHA} values for bridged di- and triarylmethanes (ref 6).

have shown that aliphatic alkyl groups alone cannot be used to establish a meaningful $\rho\sigma^*$ or $\rho\sigma_I$ relationship. Their results spectacularly confirm the earlier analysis of Ritchie and Sager[5] that the polar effect of alkyl groups does not differ from that of methyl. We have long been wary of basing polar effect correlations on alkyl groups alone and have generally incorporated the benzyl group in our series. The benzyl group has a well-defined polar substituent constant and should lead to reasonable conclusions regarding the role of polar effects. Hence, the above derivation of the polar effect in 9-phenylfluorene should not be far in error.

In an alternative derivation of this number we recall that the phenyl substituent in the anion derived from 10-phenyl-9,9-dimethyl-9,10-dihydroanthracene (PDDA) is essentially nonconjugating. For example, the p-biphenylyl group is only 0.3 pK units more acidifying in this system than the phenyl group itself (Figure 1).[6] This small effect may be compared with the ΔpK of 2.2 reported for toluene and p-methylbiphenyl.[7,8] Hence, the pK_{CsCHA} difference of 2.3 between the phenyl compound PDDA and the methyl derivative 9,9,10-trimethyl-9,10-dihydroanthracene, TDA, may be associated with the polar effect difference of an essentially nonconjugating phenyl and a methyl substituent. A similar ΔpK_{CsCHA} of 2.0 is found for phenyl and methyl substituents on dibenzocycloheptadiene (Figure 1) in which phenyl conjugation is still more restricted. If a ΔpK of this magnitude is applied to the pK_{CsCHA} of 22.3 for 9-methylfluorene, we derive a pK of about 20 for the hypothetical PF with a nonconjugating phenyl group. Hence, both independent approaches give comparable values. These values are only 1–1.5 pK units higher than the pK_{CsCHA} of 18.49 associated with PF itself and indicate that the phenyl in this system is only weakly conjugating. Weak conjugation is also indicated by the fact that 9-p-biphenylylfluorene is only 0.4 pK units more acidic in aqueous Me_2SO than PF itself.[9] From a more detailed study of phenyl substituent effects on equilibrium acidities of 9-arylfluorenes, Cockerill and Lamper[9] concluded that the phenyl group was seriously twisted and that conjugation effects were only partially transmitted to the 9-fluorenyl position. Bordwell et al.[10] have also recently discussed the variable role of phenyl groups on the equilibrium acidities of carbon acids.

In order to evaluate the effect of a fully coplanar and conjugating phenyl group in the 9-phenylfluorenyl π system, we prepared the hydrocarbon 8,8-dimethyl-8,12b-dihydrobenz[a]fluoranthene (DDF), in which a *gem*-dimethylmethylene group bridges the ortho position of the phenyl and the 1-fluorenyl position of a 9-phenylfluorene. The synthesis was straightforward and is outlined in Chart I. The spectrum of the cesium salt was obtained in CHA and was used to obtain the pK_{CsCHA} of the hydrocarbon by reference with 1,12-(o-phenylene)-7,12-dihydropleiadene (PDP), whose pK_{CsCHA} has been determined previously to be 15.36.[11] The value thus obtained for the pK_{CsCHA} of DDF is 15.45 ± 0.13.

In the anion from DDF, models show clearly that the phenyl group is locked into effective coplanarity with the fluorenyl anion. In order to use its pK value to estimate a value for a hypothetical 9-phenylfluorenyl system with a strain-free coplanar phenyl we need to assess the relative contributions of strain effects in DDF, the polar effect of the bridge, and the rotational entropy effect.[6] No accurate assessment of the strain effect is feasible but it is likely to be relatively small, particularly since some of the strain components are common to the hydrocarbon and its anion. Note that DDF can also be viewed as a dihydroanthracene derivative with an o-phenylene group bridging the anthracene 1 and 9 positions. It seems most likely that DDF is slightly more acidic than an equivalent hypothetical strain-free system.

The rotational entropy effect results from the circumstance that the phenyl group in 9-phenylfluorene has some rotational mobility which is reduced in the anion. In DDF the bridge freezes such rotational motion in both carbon acid and carbanion. This effect operates to make 9-phenylfluorene less acidic than it would be in the absence of this effect. For a freely rotating phenyl group in the carbon acid the effect has been estimated to be roughly 1 pK unit; the effect is less if the phenyl group has partially restricted rotation in the carbon acid as is probably the case for 9-phenylfluorene. That is, we expect that the rotational entropy effect by itself would suggest a pK_{CsCHA} corresponding to our hypothetical planar 9-phenylfluorenyl anion as several tenths units higher than DDF.

Finally, we consider the polar effect of the alkyl bridge in DDF. From ring-substituent effects on acidities of fluorene[12] and phenyl substituent effects on 9-phenylfluorene, [9]we estimate the effect of the dimethylmethylene bridge to be somewhat less than 1 pK unit; hence, the hypothetical coplanar 9-phenylfluorenyl anion which has no substituents would be lower than DDF by this magnitude. Thus, we find that the strain and rotational entropy effects are expected to cause a pK change in the opposite direction to and of comparable magnitude to the alkyl substituent effect of the bridge.

The foregoing analysis suggests that the pK_{CsCHA} corresponding to a hypothetical strain-free planar 9-phenylfluorenyl anion is about 15.5, or 7.5 units lower than fluorene itself. Compared to the value of 19.5–20 derived above for a 9-phenylfluorenyl system in which the phenyl group exerts only a polar effect, we derive a 4–4.5 pK unit effect for conjunction itself. This result of a 2.5–3 pK unit polar effect and a 4–4.5

pK unit conjugation effect may be compared with our earlier comparison[13] of triphenylmethane and triptycene wherein we concluded that roughly one-third of the greater ion pair acidity of triphenylmethane relative to cyclohexane was due to a polar effect. Note that this 2:1 ratio of conjugation to polar effects is substantially smaller than the ~4:1 ratio estimated by the Bordwell group[10] for 9,10-dihydroanthracene and xanthene in Me$_2$SO.

An interesting application of the present result involves additional comparison with the pK_{CsCHA} of 17.26 determined previously[11] for 8,9,13b-trihydrotribenzo[*a*,*cd*,*h*]azulene (bishomofluoradene, BHFD). This hydrocarbon is a 9-phenylfluorene with an ethano bridge between the phenyl and the fluorene. Dreiding models indicate that in the carbanion derived from BHFD the phenyl group is locked at an angle of about 30° relative to the fluorenyl plane. The three points now available for 9-phenylfluorenyl systems (0°, 15.5; 30°, 17.3; 90°, 19.5–20) form a smooth curve in which interpolation of the pK_{CsCHA} of real PF corresponds to a twist angle of about 50°. This value is somewhat higher than earlier and cruder estimates.[9,14]

Finally, we point to an interesting comparison with some recent work of the Bordwell group.[10] In Me$_2$SO, acetone and acetophenone have pK values of about 25 and they showed that a phenyl substituent increases the acidity of each compound by about 7 pK units. These compounds are sufficiently free of steric effects that the phenyl group is expected to conjugate fully. Fluorene has about the same pK value and we have now shown that a fully conjugating phenyl also has about a 7 pK unit acidifying effect. This finding gives added justification to their proposed correlation between the pK of a parent acid and the phenyl group substituent effect, at least for delocalized carbanions. Indeed, this correlation may provide a significant new tool for establishing the localized or delocalized nature of carbanions.

Experimental Section

8,8-Dimethyl-8,12b-dihydrobenz[*a*]fluoranthene (DDF). 9-(*o*-Carboxyphenyl)fluorene[15] was esterified with diazomethane in ether at 0 °C. Alternative methods of esterification failed to give the desired compound.[16] To a Grignard solution prepared by adding 12.5 mL (0.2 mol) of methyl iodide to 4.89 g (0.202 mol) of magnesium in 40 mL of ether held at reflux for 1.5 h was added a solution of 6.05 g (0.020 mol) of 9-(*o*-carbomethoxyphenyl)fluorene in benzene diluted with ether. After 0.5 h, the burgundy red solution turned opaque and the solid magnesium salt of the alcohol precipitated out of the solution. After further reflux for 2 h, the reaction was worked up with saturated ammonium chloride and ether extraction. The dried extract yielded 4.04 g (67%) of *o*-(9-fluorenylphenyl)dimethylcarbinol, mp 160–163 °C (cyclohexane).

Anal.[17] Calcd for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 87.9; H, 6.6.

To 70 mL of distilled trifluoroacetic acid was added 0.515 g (1.72 mmol) of the above carbinol. The solution was refluxed for 2 h, cooled to room temperature, and poured into a separatory funnel containing ether and water. The ether layer was washed with dilute potassium carbonate and then water. Evaporation of the dried ether extract gave an oil which was dissolved in a minimum amount of benzene and streaked onto two 20 × 20 cm, 2.0-mm thick fluorescent preparative TLC plates (Brinkman Instruments, Inc.). The plates were developed three times using 5% benzene–hexane. The fastest moving strip was extracted in a Sohxlet extractor with ether. Removal of the ether under reduced pressure left a light yellow oil which crystallized from benzene–ethanol as fine white needles, mp 102–104 °C, 0.289 g (60%).

Anal.[17] Calcd for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.4; H, 6.4.

Other carbonium ion ring-closure attempts failed to give the desired hydrocarbon.[16]

Spectral and Equilibrium Measurements. The apparatus and procedure for spectral and equilibrium measurements at room temperature have been described previously.[18,19] The spectrum of DDF as measured on a Cary 118 spectrophotometer is: λ_{max} (ϵ) 528 (2538), 500 (3062), 470 nm (sh).

The indicator used on the DDF equilibrium runs was 1,12-(*o*-phenylene)-7,12-dihydropleiadene (PDP) which was prepared from material supplied by Professor P. T. Lansbury.[20] Its spectrum has been reported previously.[11] The equilibrium between these cesium salts was measured in five runs[16] with the concentration ranges: DDF, $5\text{–}10 \times 10^{-4}$ M and its cesium salt $1\text{–}4 \times 10^{-4}$ M; PDP, $1\text{–}4 \times 10^{-3}$M and its cesium salt $4\text{–}12 \times 10^{-4}$ M. The equilibrium constant for PDPCs + DDF ⇄ DDFCs + PDP is 0.83 ± 0.25, corresponding to a pK_{CsCHA} for DDF of 15.45 ± 0.13 (stand dev).

Registry No.—DDF, 64611-29-6; 9-(*o*-carboxyphenyl)fluorene, 64611-30-9; diazomethane, 334-88-3; methyl iodide, 74-88-4; 9-(*o*-carbomethoxyphenyl)fluorene, 64611-31-0; *o*-(9-fluorenylphenyl)-dimethylcarbinol, 64611-32-1; trifluoroacetic acid, 76-05-1.

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