1-(3,4-Dimethoxybenzyl)-1,2,3,4-tetrahydroisoquinoline Hydrochloride (1d HCl). A solution of 4 g (6.6 mmol) of **1c** in 200 ml of acetic acid was hydrogenated at 50 psi in the presence of 2 g of 10% Pd/C at 40 °C in a Parr apparatus for 17 h and filtered. The filtrate was evaporated, the residue distributed between a mixture of 100 ml of 2 N hydrochloric acid and ethyl acetate, and the organic layer washed with 100 ml of water. The aqueous layers were combined, rendered alkaline with 10% sodium hydroxide, and extracted with ethyl acetate, and the organic phase was acidified with ethanolic hydrogen chloride, and evaporated. The residue was crystallized from a mixture of ethanol and ether to give 1.7 g (80%) of **1d** HCl, mp 228–230 °C, identical in mixture melting point, TLC, and NMR with authentic **1d** HCl.[4]

2,3-Bis(1-phenyl-1*H*-tetrazol-5-yloxy)-9,10-dimethoxy-5,6,13,13a-tetrahydro-8*H*-dibenzo[*a,g*]quinolizine Hydrobromide (2c HBr). To a solution of 6.8 g (20 mmol) of (±)-canadine[6] (**2a**) in 200 ml of methylene chloride at room temperature was added 48 ml of a methylene chloride solution containing 4.8 g (40 mmol) of boron trichloride. After storage overnight, 50 ml of methanol was added over 15 min, the mixture evaporated, and the residue crystallized from methanol to give 5.8 g (80%) of 2,3-dihydroxy-9,10-dimethoxy-5,6,13,13a-tetrahydro-8*H*-dibenzo[*a,g*]quinolizine hydrochloride (**2b** HCl): mp 259–261 °C; NMR δ 2.6–3.7 (m, 8, 4 CH_2), 3.77, 3.79 (2 s, 6, 2 OCH_3), 4.2–4.8 (m, 1, CH), 6.08 (s, 1, aromatic), 6.15 (s, 1, aromatic), 7.01 (s, 2, aromatic), 8.91, 9.15 (b, 2, 2 OH).

Neutralization of the above hydrochloride followed by acidification with hydriodic acid and crystallization from methanol afforded **2b** HI, mp 200–202 °C (lit.[7] mp 201–203 °C).

In a manner similar to the procedure for **1c** HCl, 3.3 g (10 mmol) of **2b** HCl, 4 g (20 mmol) of 5-chloro-1-phenyl-1*H*-tetrazole and 4.5 g (33 mmol) of anhydrous potassium carbonate in 200 ml of acetone afforded 6.5 g (95%) of **2c** HBr: mp 205–207 °C (from acetonitrile); NMR δ 2.9–4.2 (m, 6, 3 CH_2), 3.80 (s, 6, 2 OCH_3), 4.2–5.2 (m, 3, CH_2 + CH), 7.04 (s, 2, aromatic), 7.50, 7.53 (2 s, 10, aromatic), 7.84, 8.02 (2 s, 2, aromatic).

Anal. Calcd for $C_{33}H_{29}N_9O_4$·HBr: C, 56.90; H, 4.34; N, 18.10. Found: C, 56.89; H, 4.33; N, 18.35.

9,10-Dimethoxy-5,6,13,13a-tetrahydro-8*H*-dibenzo[*a,g*]quinolizine Hydrochloride (2d HCl). By the procedure given for the preparation of **1d** HCl, 10 g (16 mmol) of **2c** in 200 ml of acetic acid was hydrogenated in the presence of 3 g of 10% Pd/C to give 3 g (64%) of **2d** HCl: mp 234–235 °C (from ethanol); NMR δ 2.7–3.9 (m, 6, 3 CH_2), 3.76, 3.78 (2 s, 6, 2 OCH_3), 4.45 (b, 3, $^+NCH_2C_6H_5$ + CH), 6.99 (s, 2, aromatic), 7.24 (s, 2, aromatic), 7.38 (b, 2, aromatic), 12.0 (b, 1, NH^+).

Anal. Calcd for $C_{19}H_{21}NO_2$·HCl: C, 68.77; H, 6.68; N, 4.22. Found: C, 68.54; H, 6.69; N, 4.35.

(+)-1(*R*)-1-[3(*S*)-6,7-Dimethoxyphthalidyl]-2-methyl-6,7-bis(1-phenyl-1*H*-tetrazol-5-yloxy)-1,2,3,4-tetrahydroisoquinoline (3c). In a manner similar to the procedure for **1c** HCl, 11 g (30 mmol) of (+)-1-(*R*)-[6,7-dimethoxy-3-(*S*)-phthalidyl]-6,7-dihydroxy-2-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride[2] (**3b** HCl), 12 g (66 mmol) of 5-chloro-1-phenyl-1*H*-tetrazole, and 9 g (66 mmol) of anhydrous potassium carbonate in 600 ml of acetone provided, after crystallization from ethyl acetate, 16.7 g (85%) of **3c**: mp 162–163 °C; $[\alpha]_D$ +9.0° (*c* 0.5, $CHCl_3$); NMR ($CDCl_3$) δ 2.20–3.36 (m, 4, CH_2CH_2), 2.60 (s, 3, NCH_3), 3.9, 4.03 (2 s, 3 each, 2 OCH_3), 4.08, 5.58 (AB, 2, J_{vic} = 4 Hz, CHCH), 6.86, 7.18 (AB, 2, J_{ortho} = 8.5 Hz, aromatic), 7.18 (s, 1, aromatic), 7.39, 7.43 (2 s, 10, aromatic), 7.56 (s, 1, aromatic); uv max 220 nm (ε 53 000), 235 (11 900) (infl), 278 (2700) (infl), 310 (4400); ORD (*c* 0.659, 50% MeOH in 0.1 N HCl) $[\phi]_{650}$ +920°, $[\phi]_{589}$ +320°, $[\phi]_{250}$ +75 000° (pk), $[\phi]_{218}$ −300 000° (tr); CD (*c* 0.659, 50% MeOH in 0.1 N HCl) $[\theta]_{348}$ 0, $[\theta]_{318}$ −3200, $[\theta]_{290}$ 0, $[\theta]_{276}$ +11 500, $[\theta]_{232}$ +232 500, $[\theta]_{219}$ 0, $[\theta]_{205}$ −290 000, $[\theta]_{200}$ −185 000.

Anal. Calcd for $C_{34}H_{29}N_9O_6$: C, 61.91; H, 4.43; N, 19.11. Found: C, 62.03; H, 4.36; N, 19.23.

(−)-1-(*R*)-[3(*S*)-6,7-Dimethoxyphthalidyl]-2-methyl-1,2,3,4-tetrahydroisoquinoline (3d). By the procedure given for the preparation of **1d** HCl, 7 g (10 mmol) of **3c** in 200 ml of acetic acid was hydrogenated in the presence of 3 g of 10% Pd/C to give, after crystallization from a mixture of ether and petroleum ether (bp 30–60 °C), 3.1 g (90%) of **3d**: mp 89–90 °C; $[\alpha]_D$ −27.4° (*c* 0.5, $CHCl_3$); NMR ($CDCl_3$) δ 2.10–3.00 (m, 4, CH_2CH_2), 2.56 (s, 3, NCH_3), 4.00 (2 s, 3 each, 2 OCH_3), 4.10, 5.52 (AB, 2, J_{vic} = 4 Hz, CHCH), 6.28, 7.00 (AB, J_{ortho} = 8.5 Hz, aromatic), 6.90 (m, 1, aromatic), 7.12 (m, 3, aromatic); uv max 209 nm (ε 36 500), 263 (1130) (sh), 272 (1150), 310 (4150); ORD (*c* 0.679, MeOH) $[\phi]_{650}$ +220°, $[\phi]_{589}$ +275°, $[\phi]_{420}$ +510°, $[\phi]_{400}$ +520°, $[\phi]_{380}$ +470°, $[\phi]_{305}$ +5300°, $[\phi]_{294}$ +7400° (pk), $[\phi]_{283}$ +7100° (tr), $[\phi]_{231}$ +45 000° (pk), $[\phi]_{209}$ −137 500° (tr); CD (*c* 0.679, MeOH) $[\theta]_{365}$ 0, $[\theta]_{315}$ −6500, $[\theta]_{285}$ −1000, $[\theta]_{258}$ −4100, $[\theta]_{250}$ 0, $[\theta]_{236}$ +35 000, $[\theta]_{220}$ +118 750, $[\theta]_{207}$ 0, $[\theta]_{200}$ −81 250.

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.55; H, 6.27; N, 4.03.

Acknowledgments. We wish to thank the following members of our Physical Chemistry Department (Director, Dr. R. P. W. Scott): Dr. F. Scheidl for the microanalyses, Dr. T. Williams for the NMR spectra, and Dr. V. Toome for the uv, ORD, and CD spectra.

Registry No.—**1b** HCl, 19384-75-9; **1c**, 58298-39-8; **1c** HCl, 58298-40-1; **1d** HCl, 3972-77-8; **2a**, 29074-38-2; **2b** HCl, 58298-41-2; **2b** HI, 58298-42-3; **2c**, 58298-43-4; **2c** HBr, 58298-44-5; **2d** HCl, 58298-45-6; **3b** HCl, 58298-46-7; **3c**, 58298-47-8; **3d**, 58298-48-9; 5-chloro-1-phenyl-1*H*-tetrazole, 14210-25-4.

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Proton Transfer from the Monoanion of 1,1-Cyclopropanedicarboxylic Acid

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Hydrogen bonding in the monoanions of dicarboxylic acids has received much study since Brown and McDaniel suggested that extraordinarily high K_1/K_2 ratios arise from it.[1] Eberson and Wadsö[2] concluded that it is responsible for ratios greater than about 10 000, and Dygert, Muzii, and Saroff[3] proposed that it might be important in compounds with ratios larger than 1200.

Proton transfer rates confirm this interpretation. Eyring and co-workers have studied two families of dicarboxylic acids, and found that the rate of proton removal by hydroxide ion from the monoanion is inversely related to the strength of the hydrogen bond.[4] With dialkyl substituted malonic acids, the hydrogen bond strength is seemingly closely related to the bulk of the substituent groups. The diisopropyl compound has the greatest K_1/K_2 ratio and the smallest k_f for proton removal. It was suggested that spreading the angle between the alkyl groups results in decreasing the angle between the carboxyl groups, and that "closing the jaws" produces a stronger hydrogen bond.[4b]

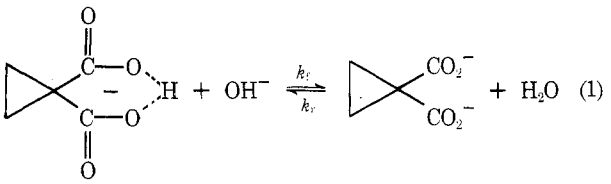
In this connection, a study of 1,1-cyclopropanedicarboxylic acid seemed of interest. X-ray crystallography has re-

Table I. Calculated Rate Constants, 25 °C, μ = 0.1 M (KNO_3)

pH	Total acid[a] × 10^4	Total indicator[b] × 10^6	$\tau \times 10^4$, s[c]	$k_f \times 10^{-8}$, l./mol s uncorr[d]	α[e]	$k_f \times 10^{-8}$, l./mol s corr[f]
8.14	2.610	5.439	2.65	1.07	1.10	2.17
8.33	5.150	8.000	1.91	1.11	1.06	2.20
8.37	5.150	12.23	2.06	1.11	1.47	2.57
8.37	5.150	17.29	2.02	1.13	2.08	3.18
8.39	5.150	10.299	2.09	1.14	1.17	2.33
8.44	2.610	5.439	3.72	1.31	0.54	1.90
8.52	5.208	4.786	2.62	1.14	0.38	1.53
8.62	5.208	2.393	2.73	1.31	0.14	1.47
8.66	2.604	4.786	3.89	1.72	0.24	2.02
8.69	2.604	8.000	3.83	1.80	0.37	2.25
8.80	2.083	2.393	4.48	1.93	0.08	2.01
8.84	2.604	2.393	4.08	1.89	0.07	1.96
8.84	1.572	2.393	4.46	2.25	0.07	2.31

[a] Total acid = $[A^{2-}] + [HA^-] + [H_2A]$. [b] Cresol red; p$K$ (μ = 0.1) = 8.20 (ref 4b). [c] Each relaxation time is an average of at least three runs. [d] Calculated from eq 4. [e] Correction factor defined in eq 2. [f] Calculated from eq 2.

vealed an angle of 118.3° between the carboxyl groups in this compound,[5] as contrasted to a corresponding angle of 110° in malonic acid.[6] This angle should be even less in the disubstituted malonic acids. The results of a temperature jump study of eq 1 are presented here.



(1)

Experimental Section

1,1-Cyclopropanedicarboxylic acid was prepared by saponification of the commercially available (Aldrich) diethyl ester. Recrystallization from ethyl acetate–petroleum ether (bp 36–60 °C) gave white crystals, mp 140–140.5 °C (lit.[7] mp 136 °C). All other reagents were commercially available reagent grade materials that were used without further purification.

Solutions for measurement were prepared by mixing appropriate aliquots of 1.0 M potassium nitrate, ~1 × 10^{-2} M 1,1-cyclopropanedicarboxylic acid, and ~1 × 10^{-4} M indicator solution, and diluting with distilled, demineralized, freshly boiled water. The pH was adjusted by addition of a few drops of ~0.1 N sodium hydroxide. Stock solutions of cresol red were prepared in 95% ethanol. Final solutions thus contained ~0.5% (volume) ethanol, which was shown to have no effect on the heating time constant, and were 0.1 M in potassium nitrate. Final concentrations are shown in Table I. A portion of the solution for measurement was transferred to a tightly capped vial and thermostatted at 25 °C. The pH was recorded by means of a calibrated Orion 801 digital meter and a Sargent combination electrode. The remainder of the solution was thermostatted at 18 °C prior to the temperature jump experiment.

Temperature jump measurements were performed at 573 nm, the λ_{max} for cresol red, with a Durrum Instruments Model D-150 rapid kinetics spectrophotometer. Nominal jumps of 7 °C were effected. All analyses gave correlation coefficients of better than −0.99. Each relaxation time reported is the average of at least three measurements. The individual runs usually agreed to better than ±7%, and never exceeded ±15% deviation from the mean.

"Mixed" ionization constants were determined potentiometrically using a glass electrode and a calomel reference in solutions prepared so that μ = 0.1 M (potassium nitrate) at the midpoint of the titration.[8] Calculations were done as outlined by Albert and Serjeant.[9] Duplicate runs to establish pK_1^M using carbonate-free 0.1 N potassium hydroxide showed a scatter of ±0.02 pK units, while triplicate runs for pK_2^M using carbonate-free 1.0 N potassium hydroxide gave a scatter of ±0.01 pK units.

Results and Discussion

German, Jeffrey, and Vogel reported thermodynamic pK values of pK_1^T = 1.82 and pK_2^T = 7.43 for 1,1-cyclopropanedicarboxylic acid.[10] The corresponding values of the "mixed" pK's at μ = 0.1 M have now been found to be pK_1^M = 1.61 ± 0.02 and pK_2^M = 7.316 ± 0.01. The K_1/K_2 ratio ("mixed" constants) is therefore 509 000.

Rate constants for the forward reaction of eq 1 were evaluated using the coupled indicating equilibrium technique that has been detailed by Eigen and Kruse,[11] and elaborated by Eyring and co-workers.[4] The expression relating reaction time to rate constant is given in eq 2

$$\tau^{-1} = k_f([HA^-]/(1 + \alpha) + [OH^-] + K_w/K_2) \quad (2)$$

in which K_w is the ion product of water, K_2 is the second ionization constant of the acid, and α is the correction term $[HIn^-]/(K_w + [OH^-])$. The correction term allows for the perturbation of the coupled indicating equilibrium shown in eq 3

$$HIn^- + OH^- \rightleftharpoons In^{2-} + H_2O \quad (3)$$

and K_{In} refers to the equilibrium constant for this reaction. As has been noted,[4b,11] when α is small (<~0.5) the correction is small; but as α increases there is an apparent tendency for overcorrection. The uncorrected rate constants obtained from eq 4

$$\tau^{-1} = k_f([HA^-] + [OH^-] + K_w/K_2) \quad (4)$$

were shown to be satisfactory with two families of compounds.[4]

Table I contains the results of 13 runs made using a variety of concentrations. That the calculated rate constants belong to eq 1 can be inferred from the lack of indicator effects on the relaxation time. Entries 2–5 represent runs at constant total acid and pH with varying indicator concentrations. The relaxation times for these runs agree quite closely, however, suggesting that the indicator is not involved in the rate-determining step. The slight upward drift of the uncorrected rate constants as the pH is increased is thought to be insignificant, considering the wide variations of concentrations employed. The monoanion to hydroxide ion concentration ratio ranges from 32.7 at the lowest pH to 0.87 at the highest.

The best value of k_f can be obtained by use of eq 4. A plot for all points of $1/\tau$ vs. $[HA^-] + [OH^-]$ gives a straight line (correlation coefficient = 0.989) with least-squares slope of 8.0 × 10^7 l./mol s. In close agreement, a plot of $1/\tau$ vs. $[HA^-]/(1 + \alpha) + [OH^-]$ (eq 2), using the eight points for which $\alpha < 0.55$, gives a straight line (correlation coefficient = 0.987) with slope of 9.0 × 10^7 l./mol s. The inclusion of all points in this latter plot results in a correlation coefficient

of only 0.722, indicating once again the inadequacy of the correction term when it is large.

Both the K_1/K_2 ratio and the k_f value place 1,1-cyclopropanedicarboxylic acid in the same position within the series of substituted malonic acids previously studied. This finding reaffirms that the K_1/K_2 ratio and the k_f value are both reflections of the hydrogen bond strength in the monoanion, but suggests that the hydrogen bond strength is not necessarily related to the angle between the carboxyl groups.

Registry No.—1,1-Cyclopropanedicarboxylic acid, 598-10-7; monoanion of 1,1-cyclopropanedicarboxylic acid, 58325-50-1.

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Preparation of 9,10-Difluoroanthracene

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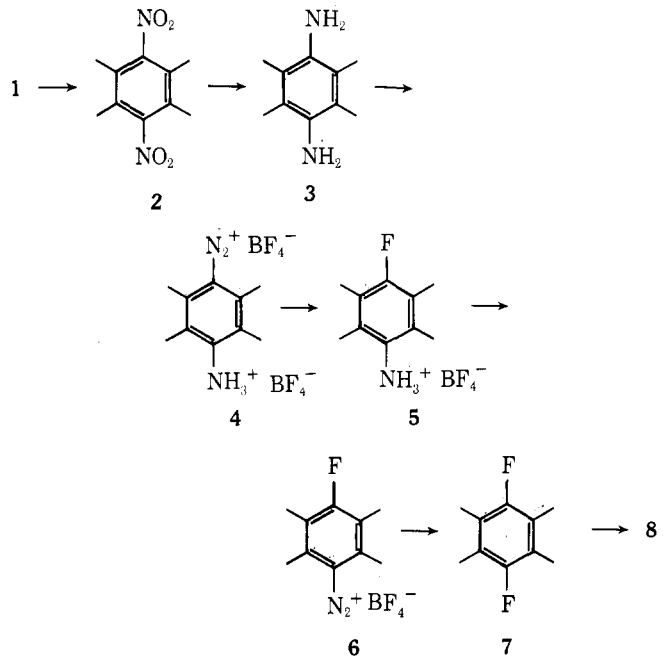
Fluoroanthracene and 9,10-difluoroanthracene are valuable molecules for investigations in magnetic resonance and photochemistry.[1,2,3] These aryl fluorides are not readily prepared by the Schiemann reaction or its modifications.[4] Thus, the first successful preparation of 9-fluoroanthracene from 9-aminoanthracene used nitric oxide as the diazotization reagent.[5] However, 9-aminoanthracene is readily oxidized and widely variable amounts of the desired diazonium salt are obtained.[6] Dewar and Michl circumvented this problem by the use of 9-amino-1,2,3,4,5,6,7,8-octahydroanthracene as the starting material for conversion to 9-fluoro-1,2,3,4,5,6,7,8-octahydroanthracene and thence to 9-fluoroanthracene by dehydrogenation.[2] However, a new difficulty arises in the application of their procedure for the synthesis of 9,10-difluoroanthracene because charged substituents in the 10 position greatly enhance the rate of hydrolysis of 1,2,3,4,5,6,7,8-octahydroanthracene-9-diazonium tetrafluoroborate.[7] We wish to report a route, Chart I, for the synthesis of 9,10-difluoroanthracene in which these hydrolysis reactions are minimized. This known compound was previously obtained in less than 1% yield as a by-product in the reaction of fluorobenzyne with furan[8] and in 5% yield by the reaction of sulfur tetrafluoride with anthraquinone to yield 9,9,10,10-tetrafluoro-9,10-dihydroanthracene followed by iron gauze catalyzed defluorination.[9]

Octahydroanthracene (1) was converted to the diamine 3 in good yield using known procedures.[10] Not unexpectedly,

Chart I



the treatment of 3 in aqueous media with nitrous acid prepared from either sulfuric, hydrochloric, or fluoroboric acid led to small yields of octahydroanthraquinone as the only isolable product. This reaction was incomplete because the salts of 3 are insoluble in the aqueous media. The use of tetrahydrofuran as a cosolvent provided the quinone in excellent yield. As noted, the diazonium ions of duridines are unstable in water;[7] this problem is compounded in the diazonium derivatives of 3 with their activating ammonium and diazo groups. We were able to circumvent this difficulty through a reduction in the polar character of the medium using ethanol as a solvent and isoamyl nitrite as the diazotization agent in the presence of excess 48% fluoroboric acid. Under these conditions, 3 was cleanly and rapidly converted to 4 which precipitated. This salt is stable and may be stored for several weeks. Salt 4 was decomposed thermally in vacuo to give 5, which is a useful intermediate for the preparation of many other fluoroanthracenes. Compound 5 was diazotized by the procedure used for 3. The product, 6, was precipitated by the addition of ether. Diazonium salt 6 is unstable and cannot be stored for more than 1 day without noticeable deterioration. Thermal decomposition of 6 in vacuo gave 7 in 90% yield. Dehydrogenation of 7 with dicyanodichloroquinone proceeded successfully to yield 57% of 9,10-difluoroanthracene.

Experimental Section

All melting points are corrected. Varian equipment was used to record the NMR spectra at 60 or 100 MHz with tetramethylsilane as an internal reference and fluorine NMR spectra at 56.4 or 94.1 MHz. Infrared and ultraviolet spectra were recorded with Beckman IR-10 and Cary 14 instruments, respectively. Octahydroanthracene (Columbia Organic Chemicals Co.) was used without further purification. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

9,10-Dinitro-1,2,3,4,5,6,7,8-octahydroanthracene (2). Chloroform (900 ml) and concentrated sulfuric acid (450 ml) were added to a flask fitted with a mechanical stirrer, thermometer, and addition funnel. The mixture was cooled to −20 °C and 100% nitric acid (27 ml) was added cautiously. A solution of octahydroanthracene (27.0 g, 0.145 mol) in chloroform (150 ml) was added dropwise to the stirred acid mixture over 30 min maintaining the temperature below −10 °C. The resulting dark red mixture was stirred for 15 min longer, poured onto ice, and extracted with chloroform (6 × 300 ml). The extracts were combined, washed to neutrality with saturated sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed in vacuo. The residue was suspended in ethanol (500 ml) and