such as 2-phenylpropionic and 2-phenylacetic acid anhydrides and 2-*p*-nitrophenylbutyric acid chloride.

Nmr Spectra.—The nmr spectrum of the colorless 2-phenylbutyric acid anhydride (diketo tautomer) gives the expected results: δ 7.05 (s, 10 H, phenyl), 3.3 (t, 2 H, methinyl), 1.8 (o, 4 H, methylene), 0.8 (t, 6 H, methyl). The results of the nmr spectra show that the rates of exchange among the tautomers were slow enough to observe each tautomer.

Spectra taken as a function of time indicate that the ratios of tautomers also change with time when the sample is maintained at the temperature of the instrument magnet (36°). If the freshly distilled anhydride is maintained at −80°, no change in tautomer composition is observed for at least 6 months, perhaps longer. Vacuum distillation of the anhydride and direct collection into an nmr tube containing carbon tetrachloride at −80° followed by warming and observing the nmr spectrum permitted the establishment of an equilibrium of approximately half and half diketo and dienol tautomers.

Chemical shift values for the various types of protons present in each tautomer are given in Table I.

TABLE I

CHEMICAL SHIFTS FOR 2-PHENYLBUTYRIC ACID ANHYDRIDE

	Type of proton (in CCl_4, ppm)			
Tautomer	Methyl	Methylene	Methinyl	Enol OH
Diketo	0.8	1.8	3.3	
Keto half of keto–enol	0.9	1.9	3.4	
Enol half of keto–enol	1.2	2.3		11.5
Dienol	1.2	2.3		11.5

Infrared Spectra.—In addition to the normal peaks observed in the infrared for the anhydride, the peaks described below underwent changes with time. Observations of infrared spectra of the freshly distilled anhydride as a function of time showed a broad peak at 3000 cm^{-1} that disappeared rapidly, a peak at 1700 cm^{-1} that disappeared more slowly than the one at 3000 cm^{-1}, and a strong, sharp peak at 2100 cm^{-1} that disappeared at the same rate as the one at 1700 cm^{-1}. The peak at 1700 cm^{-1} is due to the carbonyl in the keto half of the keto–enol tautomer. The broad peak at approximately 3000 cm^{-1} suggests intermolecular hydrogen bonding between dienol and diketo molecules. Perhaps the most interesting peak is the one at 2100 cm^{-1} because of its relative strength and position within the spectral region. At the present time no specific assignment can be made for this peak.

Experimental Section[13]

2-Phenylbutyric acid anhydride was prepared from the reaction of the sodium salt of 2-phenylbutyric acid with 2-phenylbutyryl chloride according to accepted procedures. Vacuum distillation [70° (0.02 mm)] of the anhydride was accomplished using a Nester-Faust Annular Teflon spinning band column. The collection apparatus permitted immediate sampling of the distillate and subsequent recording of nmr and ir spectra In some cases, collection was made directly into nmr tubes onto the solid solvent at −80°.

Registry No.—2-Phenylbutyric acid anhydride (diketo), 1519-21-7; 2-phenylbutyric acid anhydride (keto–enol), 35046-01-6; 2-phenylbutyric acid anhydride (dienol), 35046-02-7.

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[13] Nmr spectra were taken on a Varian A-60A spectrometer in carbon tetrachloride with TMS as an internal standard. Infrared spectra were taken on Beckman IR-10 and Perkin-Elmer 137B spectrophotomers.

Magnetic Shielding of Acetylenic Protons in Ethynylarenes

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A number of studies of the nuclear magnetic resonance spectra of monosubstituted acetylenes, with particular emphasis on chemical shifts, have been reported in the literature.[1-4] These investigations mainly dealt with the effects of substituents,[1] the intermolecular interactions, and solvent anisotropy on the chemical shifts of acetylenic protons.[2,3] In general, alkyl substituents increase the shielding of the acetylenic protons while phenyl group largely decreases the shielding.[1] The decrease in shielding is attributed to the distortion of the π system of the acetylenic bond by the inductive effect,[4] or accounted for by the counteracting effect of the ring current by the phenyl moiety on the diamagnetic shielding of the cylindrical π-electron cloud of the triple bond.[5]

In the course of study on another problem, we have had occasion to prepare several ethynylarenes. In order to investigate further the effects of the aromatic nuclei on the diamagnetic shielding of the acetylenic proton, we have studied the nmr spectra of the acetylenic protons in ethynylarenes. The chemical shifts of the acetylenic protons of ethynylarenes are listed in Table I. These values were determined at a concentration of 0.015–0.020 mol fraction solute in CCl_4. The chemical shifts are reported in hertz and τ below TMS.

TABLE I

CHEMICAL SHIFTS OF THE ACETYLENIC PROTONS OF ETHYNYLARENES

		Chemical shift			
No.	Compd	Hz	τ	ΣR^{-3}	ΣIR^{-3}
1	Phenyl	183	6.95	0.02567	0.02567
2	2-Naphthyl	190	6.83	0.03144	0.03426
3	1-Naphthyl	201	6.65	0.03939	0.04293
4	1-Pyrenyl	214	6.43	0.04733	0.05612
5	9-Anthryl	220	6.32	0.05221	0.06157

The effects of substituents on the chemical shift of the acetylenic proton in phenylacetylene have been extensively investigated, and correlations between the

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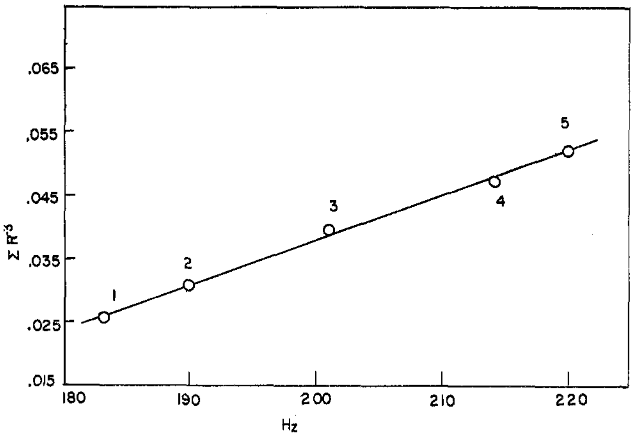

Figure 1.—Relationship between the chemical shift of acetylenic protons and ΣR^{-3}.

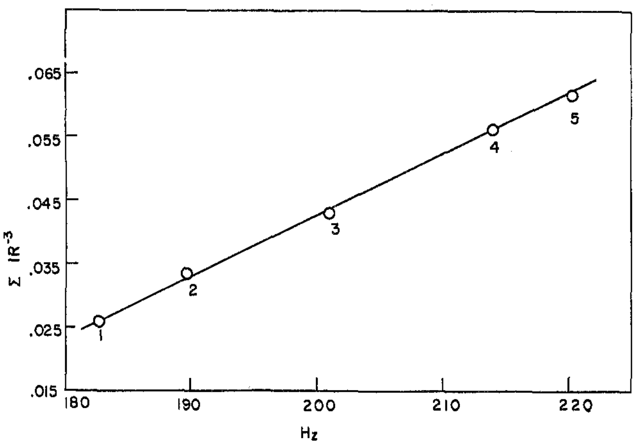

Figure 2.—Relationship between the chemical shift of acetylenic protons and ΣIR^{-3}.

chemical shifts and inductive (σ_I) and resonance (σ_R) parameters were empirically demonstrated. Strongly electron-donating substituents lead to an increase in shielding of the acetylenic proton, whereas electron-withdrawing substituents decrease the shielding. This phenomenon was simply explained by the changes of electron distribution in the ground state brought about by substituents transmitted to the acetylenic side chain.[6] Of the compounds studied in the present work, the electron density at the carbon to which the acetylene group is attached increases as shown by the following sequence.[7]

9-anthryl > 1-pyrenyl > 1-naphthyl > 2-naphthyl > phenyl

However, the shielding of the acetylenic proton in the above series was found to be in the reverse order. This observation suggests that the determinative factor in the chemical shifts of the ethynyl protons is the ring current of the different aromatic nuclei. The proton in phenylacetylene is located at a distance of 5.08 Å from the center of the phenyl ring. Our calculations based on Johnson and Bovey's[8] work showed a shift of 0.22 ppm due to the direct effect of ring current on the chemical shift of the acetylenic proton through space. This may be compared to the difference of 1.2 ppm observed between acetylene and phenylacetylene.

The magnitude of the chemical shift of the ring-bound protons in aromatic hydrocarbons is expressed by eq 1.[2] The term R is the distance from the center

$$\Delta\delta = \frac{-e^2a^2}{2mc^2R^3} \qquad (1)$$

of the ring to the affected proton. Ouellette and van Leuwen have reported the chemical shifts of the methyl group of methyl arenes.[9] A good correlation was found between the chemical shifts of the methyl protons and the summation of the inverse cubes of the distances which separate the methyl groups and the centers of the aromatic rings.

A point dipole model for ethynylarenes was used to correlate the observed chemical shifts and the distance R separating the acetylenic bonds and the center of each aromatic ring. A half-bond distance (0.6 Å) of acetylenic bond was employed and all distances reported in this paper were determined by projections of Drieding models on paper. The data are shown in Table I, in which I is the ring current intensity,[10] which increases with the increase in number of rings and is a function of molecular structure. The chemical shift of the acetylenic protons plotted against ΣR^{-3} and ΣIR^{-3} are shown in Figures 1 and 2, respectively. Excellent correlations are obtained and slopes are given by eq 2 and 3 with the correlation coefficients $r = 0.991$ and 0.998, respectively.

$$\delta = 1408.3\Sigma R^{-3} + 136.4 \qquad (2)$$

$$\delta = 1041.6\Sigma IR^{-3} + 155.7 \qquad (3)$$

Butadi- and hexatriynyl derivatives of 1- and 2-naphthalenes and benzene were synthesized for further studies of the effects of the ring current on the acetylenic protons. The syntheses were carried out by the coupling reactions of the corresponding copper acetylides with bromoacetylene in dimethylformamide. The nmr spectra of these compounds with the reported data of the methyl di- and triynes are summarized in Table II.

TABLE II

CHEMICAL SHIFTS OF THE ACETYLENIC PROTONS OF POLYYNES

Compd	Chemical shifts, Hz (τ)[a] $n = 1$	$n = 2$	$n = 3$
$CH_3(-C{\equiv}C-)_nH$[b]	108 (8.20)	105 (8.25)	112 (8.13)
$C_6H_5(-C{\equiv}C-)_nH$	183 (6.95)	138 (7.70)	
1-$C_{10}C_9(-C{\equiv}C-)_nH$	201 (6.65)	150 (7.50)	145 (7.58)
2-$C_{10}H_9(-C{\equiv}C-)_nH$	190 (6.83)	141 (7.65)	

[a] In CCl_4 solution. [b] P. Jouve and M. P. Simonnin, *C. R. Acad. Sci.*, **257**, 121 (1963).

In the case of the methyl polyyne system, the spectra of the acetylenic protons are not affected by the chain length. However, aromatic polyynes show large differences in chemical shifts between mono- and diynes, whereas the chemical shift for the proton beyond diyne remains constant within experimental error. These observations support the explanation that the counter-

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TABLE III

PHYSICAL CONSTANTS AND MICROANALYTICAL DATA OF POLYYNES

	Infrared absorption, cm^{-1}		Cu salt		Microanalytical data (Cu salts), %			
					Found		Calcd	
Compd	$\nu_{C\equiv CH}$	$\nu_{C\equiv C\ Cu}$	Dec pt, °C[a]	Registry no.	C	H	C	H
$C_6H_5(-C\equiv C-)_2H$	2110, 2190	2170 (broad)	170	34993-58-3	62.9	2.25	63.7	2.65
1-$C_{10}H_9(-C\equiv C-)_2H$	2195, 2210	2165	193	34993-59-4	69.0	3.50	69.8	3.74
1-$C_{10}H_9(-C\equiv C-)_3H$	2220, 2240	2180	165	34993-60-7	72.1	3.00	72.6	3.40
2-$C_{10}H_9(-C\equiv C-)_2H$	2220, 2180	2280	183	34993-61-8	69.2	3.44	69.8	3.74

[a] The decomposition temperatures were measured by a Du Pont 900 differential thermal analyzer.

acting effect of the ring current on the triple bond cloud in the ethynylarenes plays an important role for the deshielding in the acetylenic proton.

Experimental Section

Solvents and Reagents.—All solvents were dried over Drierite and distilled. 1,2-dibromoacetylene (Eastman Kodak Co.) and 1- and 2-acetylnaphthalenes (K and K Laboratories, Inc.) were purified by distillation.

Instrumental Analyses.—Nmr spectra were obtained on a Varian A-60 instrument. A Perkin-Elmer Model 237 infrared spectrophotometer was used for ir measurements. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU 60.

Preparation of Ethynylarenes.—Ethynylbenzene purchased from Aldrich Chemical Co. was purified by distillation. 1- and 2-Ethynylnaphthalenes were prepared from 1- and 2-acetylnaphthalenes, respectively, by conversion to the α-chloroethenyl derivatives and then dehydrochlorination of the chloro derivatives with ethanolic potassium hydroxide: 1-ethynylnaphthalene, bp 135° (20 mm) [lit.[11] bp 143–144° (20 mm)], ir 3300 ($C\equiv CH$), 2100 cm^{-1} ($C\equiv C$); 2-ethynylnaphthalene, bp 110° (1 mm) [lit.[12] bp 104–107° (1 mm)], ir 3300 ($C\equiv CH$), 2100 cm^{-1} ($C\equiv C$). 1-Ethynylpyrene was supplied by Professor M. Nakagawa, Osaka University, Japan.

Preparation of 9-Ethynylanthracene.—9-Acetylanthracene was prepared from anthracene in 62% yield by Friedel–Crafts acetylation, mp 76°, ir 1690 cm^{-1} ($C=O$). A mixture of 110 g (0.50 mol) of 9-acetylanthracene and 228.8 g (1.10 mol) of phosphorous pentachloride in 600 ml of dried benzene was refluxed until the evolution of hydrogen chloride gas ceased (*ca.* 20 hr). The reaction mixture was then cooled and poured over crushed ice. The organic layer was then separated and washed twice with cold water. After drying over anhydrous magnesium sulfate, it was concentrated to about 100 ml and then treated with 600 ml of petroleum ether (bp 30–60°). After the solution was kept in an icebox overnight, the crystalline solid (32 g) separated was collected by filtration and recrystallized from benzene–petroleum ether to afford 9,10-dichloroanthracene, mp 217°, mass spectrum m/e 246 (M^+), no depression in mixture melting point with an authentic sample. From the filtrate, 9-(α-chloroethenyl)-anthracene was obtained: 30 g; mp 78° (after three recrystallizations from methanol); ir 1630, 1618 ($C=C$), 928, 900, 890 cm^{-1}; pmr ($CDCl_3$) τ 3.86 (d, 1H, J_{vic} = 1.6 Hz), 4.48 (d, 1 H, J_{vic} = 1.6 Hz), 2.54, 1.60 ppm (m, 9 H); mass spectrum m/e 238 (M^+), 202.

Anal. Calcd for $C_{16}H_{11}Cl$: C, 81.34 H, 4.68. Found: C, 81.45; H, 4.73.

9-(α-Chloroethenyl)anthracene (20 g) was then added portionwise with vigorous stirring to a solution of sodium *tert*-butoxide in *tert*-butyl alcohol, prepared from 18 g of sodium, at room temperature. After 3 hr of gentle reflux, the reaction mixture was left overnight at room temperature in the dark and treated with 200 ml of methanol, followed by the addition of 600 ml of ice-water. It was then extracted thoroughly with benzene. The benzene layer was washed with water and then dried over anhydrous magnesium sulfate. After the solvent was evaporated under vacuum at 30°, the residue was extracted with 1000 ml of petroleum ether. Evaporation of petroleum ether afforded 5 g of 9-ethynylanthracene. It was further purified by recrystallization from petroleum ether as orange-red crystals: mp 110–112°; ir 3250 ($C\equiv CH$), 2130 cm^{-1} ($C\equiv C$); mass spectrum m/e 202 (M^+).

Anal. Calcd for $C_{16}H_{10}$: C, 95.05; H, 4.95. Found: C, 95.17; H, 4.97.

Preparation of Di- and Triynes.—The syntheses were carried out by coupling reactions of the corresponding copper acetylides with bromoacetylene in DMF.[13] The di- and triynes obtained (Table III) were isolated, purified, and characterized as the copper salts. Free acetylenic compounds were isolated from the copper salts by treatment with aqueous hydrochloride. The following is a typical procedure for the reaction. Bromoacetylene was generated by the reaction of 1,2-dibromoacetylene with alcoholic potassium hydroxide and was dissolved in DMF. To this DMF solution of bromoacetylene, copper 1-naphthylacetylide was added and kept in an icebox for 24 hr. The reaction mixture was poured into water and the excess bromoacetylene was allowed to escape by constant stirring. 1-Naphthyldiyne obtained was extracted with ether. The ether extract was added to CuCl and NH_4OH solution under a nitrogen atmosphere. The copper salt was filtered, washed with alcohol and acetone, and dried.

Registry No.—**1**, 536-74-3; **2**, 2949-26-0; **3**, 15727-65-8; **4**, 34993-56-1; **5**, 13752-40-4; 9-(α-chloroethenyl)anthracene, 13752-41-5.

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An Improved Synthesis of Acylated 3-Amino-3-deoxy-D-ribofuranose[1]

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In the synthesis of puromycin a lengthy preparation of the modified sugar moiety is involved and the overall yield[2] from D-xylose to the acylated 3-amino-3-deoxy-D-ribofuranose (**1**) is 5%. We have been interested in the preparation of puromycin with sulfur replacing the oxygen of the sugar ring and in the course of our thinking envisioned a shorter route to the acylated **1** which would make possible a much easier route to the synthesis of natural puromycin. Our shorter procedure leads from D-glucose to the acylated **1** in an overall yield of 29%.

Earlier this laboratory reported the synthesis of 3-azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**2**) from 1,2:5,6-di-*O*-isopropylidene-α-D-3-*O*-(*p*-tolysulfonyl)-α-D-glucofuranose.[3] When the azido compound **2** is selectively hydrolyzed at 25° with

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