0.1 *N* sodium thiosulfate to a starch end point. Total iodine, equivalent to unreacted iodine plus the iodine liberated from unreacted peroxide whenever present, was determined by conducting the analysis as described for diacyl peroxides.[19] Unreacted iodine was calculated as the difference between the two iodine titrations.

Isolation and Identification of "Hydroaromatic" Products. Reaction of Benzoyl Peroxide and Iodine in Nitrobenzene.—The mixture from a reaction of benzoyl peroxide (0.05 mol) and iodine (0.075 mol) in nitrobenzene (110 ml) (2 hr at 110°) was evaporated *in vacuo*. The residue was stirred in hexane and a trace quantity of insoluble material was filtered and washed with hexane. The insoluble component (analyzed without further purification) contained iodine in approximate agreement with that calculated for benzoyl hypoiodite addition to one double bond of dinitrotetrahydroquaterphenyl ($C_{31}H_{25}O_8N_2I$).

Anal. Calcd: C, 57.4; H, 3.89; N, 4.32; I, 19.6. Found: C, 60.8; H, 4.03; N, 4.20; I, 17.8.

The hexane filtrate was chromatographed on silica gel and eluted with benzene–petroleum ether cosolvent. A portion of the chromatographed material was further resolved by preparative gas–liquid partition chromatography into a liquid and a solid isomer but isolation, purification, and analyses of all components were not attempted in this limited effort. Both isomers showed the presence of nitro bands (1350 and 1520 cm^{-1}) and aromatic bands and each contained a strong 199 mass peak in its fragmentation pattern[20] corresponding to nitrodiphenyl. Elemental analysis for the solid isomer supports this structure but is less satisfactory for the liquid isomer.

Anal. Calcd: C, 72.35; H, 4.55; N, 7.03; Found for the solid isomer: C, 72.4; H, 4.83; N, 6.82. Found for the liquid isomer: C, 72.6; H, 5.04; N, 6.41.

Reaction of Benzoyl Peroxide and Iodine in Benzene.—Several of the reaction mixtures were filtered to collect a small amount of a black, insoluble compound. This was washed with benzene and dried. The compound contained 22.7% iodine in agreement with the calculated value (22.7%) for the product expected from a benzoyl hypoiodite addition to the olefinic diphenyltetrahydroquaterphenyl.

Registry No.—Iodine, 7553-56-2; benzoyl peroxide, 94-36-0; pelargonyl peroxide, 762-13-0; myristoyl peroxide, 3530-28-7; 3-nitrobenzoyl peroxide, 904-58-5; 4-nitrobenzoyl peroxide, 1712-84-1; *p*-methoxybenzoyl peroxide, 849-83-2; 4-iodonitrobenzene, 636-98-6; 3-iodonitrobenzene, 645-00-1.

(19) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); L. S. Silbert and D. Swern, *J. Amer. Chem. Soc.*, **81**, 2364 (1959).

(20) Mass spectral analysis by Mr. C. Dooley.

The Nuclear Magnetic Resonance Spectra of N-Acylanilines.[1] The Effect of Substituents on the Chemical Shift of the *ortho* Proton

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The shielding parameters of various substituents on benzene have been shown by Martin and Dailey[3] to be additive and have been used to predict successfully the chemical shifts of the protons on the benzene nucleus. This additivity fails for *ortho* protons on *ortho*-disubstituted benzenes. These deviations are relatively small (less than 0.5 ppm) and can occur at either higher or lower field, but in a recent study in these laboratories, the proton magnetic resonances of a series of N-acylanilines was determined and extremely large deviations were observed. It was noted, in certain cases, that one aromatic proton consistently appeared much farther downfield than expected and only appeared if the acylaniline was *ortho* substituted. This deshielding cannot be explained by analogy with any known effect and its cause was therefore investigated.

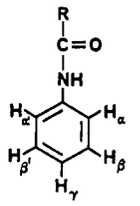

Figure 1.

Results and Discussion

The nmr spectra of a number of substituted N-acylanilines were determined and proton assignments were made where possible and when consistent with known chemical shifts. When several substituents were present, the characteristic splitting patterns were also utilized *via* first-order analysis in making assignments. The results are shown in Table I. Figure 1 details the designation of the ring protons. As can be seen from Table I, H_α consistently appears as the most deshielded proton in compounds VII–XVIII. This deshielding is minimal with unsubstituted acetanilide or when the substituents are other than *ortho*. The first six compounds in Table I contain no *ortho* substituent. The chemical shifts for aromatic protons of these compounds (I–VI) are quite close to their predicted values if either Martin and Dailey's[3] or Corio and Dailey's[4] shielding parameters are utilized. In addition it was necessary to assign a shielding parameter for the acylamino group. A calculated value of +0.16 ppm (δ scale) was determined by the analysis of several *para*-substituted acylanilines.

When a similar treatment was attempted with the *ortho*-substituted ($H_{\alpha'}$ = R) compounds (VII–XVIII), the proton *ortho* to the acylamino group (H_α) appeared farther downfield than could be reasonably explained by electrostatic effects, and the deviation of the observed chemical shifts from those calculated using shielding parameters was unusually large. Initially it was thought that the magnitude of this deshielding effect would be relatively constant regardless of the nature of the *ortho* substituent. This, however, was not the case. Using Corio and Dailey's[4] values for shielding parameters, the effects of the *ortho* substituents were subtracted from the total chemical shift difference of the *ortho* proton. This gave some measure of the magnitude of the anisotropic deshielding of the carbonyl group in the various compounds. The results are summarized in Table II. Corio and Dailey's[4] values were chosen, not because they are the most accurate but because the list of substituents is the most exten-

(1) Presented at the Symposium on the Application of Spectral Techniques to Problems of Structure and Mechanism, 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., February 1, 1968.

(2) To whom all correspondence should be addressed.

(3) J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

(4) P. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, **78**, 3043 (1956).

TABLE I
PMR PARAMETERS OF N-ACYLANILINES

		Ring substituents			Chemical shifts (δ)					Coupling constants	
RCONHAr	R	α′	β′	γ	α	β	γ	α′	β′	J_{meta}	J_{ortho}
I	CH_3	...	...	...	7.0–7.60	7.0–7.60	7.0–7.60	...	7.0–7.60	...	...
II	CH_3	...	...	F	7.40	...	...	7.40	...	...	...
III	CH_3COCH_2	...	...	CH_3	7.43	7.10	...	7.43	7.10	...	...
IV	CH_3COCH_2	...	...	EtO	7.43	6.83	...	7.43	6.83	...	...
V	$ClCH_2$	...	NO_2	...	7.90	7.50	8.06	8.44	...	2	8
VI	CH_3	...	...	NO_2	7.82	8.35	...	7.82	8.35	...	...
VII	CH_3	CH_3	...	...	7.48	7.0–7.20	7.0–7.20	...	7.0–7.20	...	...
VIII	CH_3	Br	...	CH_3	7.92	6.98	...	...	7.25	2	9
IX	CH_3	F	...	...	8.20	6.9–7.2	6.9–7.2	...	6.9–7.2	...	...
X	CH_3	OH	...	...	7.68	6.6–7.08	6.6–7.08	...	6.6–7.08	2	7
XI	CH_3	NO_2	...	...	8.74	7.11	7.61	...	8.15	2	9
XII	CH_3	NO_2	...	Br	8.76	7.75	...	...	8.38	3	9
XIII	CH_3	COOH	...	...	8.50	7.15	7.60	...	8.0	2	8.5
XIV	$ClCH_2$	NO_2	...	...	8.77	7.20	7.65	...	8.21	2	8.5
XV	$HSCH_2$	Cl	...	...	8.33	6.8–7.5	6.8–7.5	...	6.8–7.5	2	8
XVI	CH_3CH_2O	Cl	Cl	...	8.11	7.0–7.4	7.0–7.4	...	...	2	7
XVII	CH_3COCH_2	Cl	...	Cl	8.30	7.22	...	...	7.39	2	8
XVIII	$HS\text{-}CH_2$	CH_3O	...	...	8.32	6.8–7.1	6.8–7.1	...	6.8–7.1	...	...

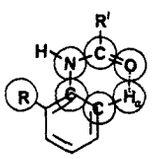

Figure 2.

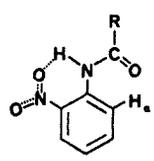

Figure 3.

TABLE II
EFFECT OF THE ANISOTROPIC DESHIELDING OF THE CARBONYL GROUP IN *ortho*-SUBSTITUTED ACYLANILINES

ortho substituent	δ H (obsd)	δ (calcd)	Δδ
CH_3	7.48	7.33	0.15
F	8.20	7.43	0.77
OH	7.68	7.06	0.62
NO_2	8.74	7.73	1.01
COOH	8.50	7.53	0.97
Cl	8.33	7.43	0.90
OCH_3	8.32	7.20	1.12

sive available. The range is seen to vary from +0.15 to 1.12 ppm, with an average value of 0.79 ppm. This *ortho* effect is therefore significant and is comparable to even the strongest electrostatic deshielding groups. The other aromatic protons in these compounds had chemical shifts which compared favorably with their predicted values.

Another, though less important observation (see Table I) was that the nature of the group attached to the acyl carbon atom had relatively little effect on the chemical shifts of the aromatic protons. As an example two *o*-nitroacylanilines (XI and XIV) have virtually identical chemical shifts for all of their aromatic protons, even though the acyl groups are different (CH_3CO– *vs.* $ClCH_2CO$–). Other examples in Table II further support this point.

Since the deshielding effect is observed only with *ortho*-substituted acylanilines, it is reasoned that at least part of the effect must be steric. The acylamino group can exist in numerous conformations with respect to the benzene ring. When there is no *ortho* substituent the time averaged paramagnetic anisotropic effect of the carbonyl group on the two equivalent *ortho* protons is relatively small (0.16 ppm). When $H_{\alpha'}$, however, is replaced by a bulkier group, the acylamine group is forced to the opposite side of the ring and fewer conformational isomers are now possible. Since the deshielding effect of the carbonyl group is so large, it is probable that only one conformation is actually present—a structure in which the nitrogen, carbonyl carbon, oxygen, *ortho* proton, and ring carbons are locked into a six-membered ring through incipient H-bonding (Figure 2). The H_α proton is now under the deshielding influence of the carbonyl group and a pronounced downfield shift is observed. Scale molecular models of these compounds support this hypothesis.

The phenomenon of anisotropic deshielding by a carbonyl group is well known,[5] and Karabatsos[6] has recently clarified the actual geometry of the shielding and deshielding zones. Models of the acylanilines would indicate that H_α does in fact lie outside the shielding zone of the carbonyl oxygen when the molecule is in the conformer described above.

As additional evidence for this explanation, it was suggested that an *ortho* substituent, which would act as a conformational lock through actual hydrogen bonding, should exhibit the "*ortho* effect" with unusual clarity. For this purpose, N-acetylanthranilic acid and *o*-nitroacetanilide were chosen. Figure 3 illustrates the hydrogen bonded structure of one of these compounds. Figure 4 depicts the nmr spectra of the *o*-nitro compound in the aromatic region. The results are apparent and each of the four aromatic protons are observ-

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 7, p 124.

(6) G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, **89**, 5067 (1967).

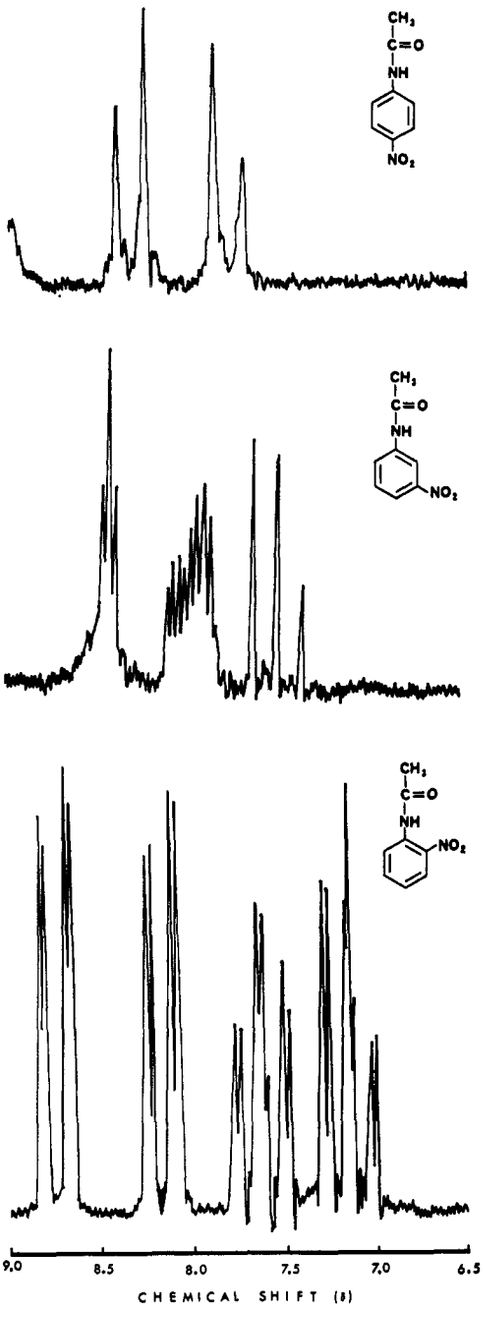

Figure 4.

able with their predicted splitting patterns. The spectra of *m*- and *p*-nitroacetanilide in the same region are also pictured for comparison. Comparing the spectra of the *o*-, *m*-, and *p*-nitroacetanilides, it can be seen that H_a in the *ortho* compound is the most deshielded aromatic proton not only in that molecule but in any compound of the series. This phenomenon has been observed for other substituents in monosubstituted acylamines.

One other interesting aspect of this study came to light when an attempt was made to extend the "*ortho* effect" to substituted phenolic esters (Figure 5). Surprisingly, there was no comparable deshielding of the H_α proton. An analysis of this unexpected result, however, now provides additional support for the original hypotheses. When scale molecular models of the acylanilines and the phenolic esters were constructed, the former were able to assume the postulated con-

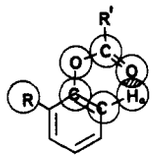

Figure 5.

formation. With the phenolic esters, however, the slight change in the C_{aryl}–O–C_{acyl} bond angle prevented a similar conformer from existing. The magnetic anisotropy of the carbonyl group, therefore, is no longer an important deshielding factor. Although other atoms can probably replace the nitrogen atom in compounds exhibiting the "*ortho* effect," the oxygen analogs cannot.

In summary, *ortho*-substituted acylanilines exhibit enhanced deshielding for the proton *ortho* to the acylamine group. The effect is a combination of the steric and electronic influence of the group *ortho* to the acylamine substituent. The bulk of the group forces the acyl carbonyl oxygen into close proximity to the *ortho* hydrogen and the electronic effect produces additional deshielding acting through the aromatic ring.

Experimental Section

The nmr spectra were obtained on a Varian Associates A-60A spectrometer operating at a frequency of 60 MHz. Samples were prepared as 10% by weight solutions in either deuterated chloroform or, in the case of difficultly soluble material, deuterated dimethyl sulfoxide. Tetramethylsilane was incorporated in the solvents as an internal standard. Normal probe temperature was 35°. The compounds investigated were obtained either from commercial sources or by synthesis. Their purity was verified by the absence of extraneous peaks in the spectra.

Registry No.—Table I: I, 103-84-4; II, 351-83-7; III, 2415-85-2; IV, 122-82-7; V, 10147-71-4; VI, 104-04-1; VII, 120-66-1; VIII, 614-83-5; IX, 399-31-5; X, 614-80-2; XI, 552-32-9; XII, 881-50-5; XIII, 89-52-1; XIV, 10147-70-3; XV, 17223-64-2; XVI, 2621-70-7; XVII, 17223-66-4; XVIII, 17223-67-5.

Fluorocarbon Difluoramines and Nitriles

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The resurgence of interest in the synthesis and reactions of nitrogen–fluorine compounds is illustrated by the fact that six review articles describing various aspects of this field have been published in the last five years.[1] In general, the most suitable methods for the synthesis of nitrogen–fluorine substituted perfluoroalkyl derivatives include fluorination of nitrogen-con-

(1) (a) J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967); (b) C. B. Colburn, *Chem. Brit.*, **2**, 336 (1966); (c) C. B. Colburn, *Endeavour*, **24**, 138 (1965); (d) C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 92 (1963); (e) A. V. Pankratov, *Usp. Khim.*, **32**, 336 (1963); (f) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962).