bridgeheads of bicyclic and tricyclic ring systems usually cause downfield shifts of the the resonances of γ-anti carbon atoms. Further examples will be required to determine the generality and reliability of this phenomenon.[20]

Experimental Section

^{13}C NMR spectra were measured at 25.15 MHz with a JEOL JNM PS-100 spectrometer interfaced with a Nova 1200 computer.[16] Compounds 8–10 were run in $CDCl_3$ solution with internal Me_4Si; compounds 11 were run in D_2O solution with external $NaO_3S(CH_2)_3Si(CH_3)_3$. With the exception of **8c**,[17,18] all of the materials employed in this study were available from previous studies or prepared according to literature procedures.[19]

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Registry No.—**8a**, 280-65-9; **8b**, 15158-56-2; **8c**, 15158-55-1; **8d**, 17530-63-1; **9a**, 491-25-8; **9b**, 56258-84-5; **9c**, 51209-45-1; **10a**, 281-05-0; **10b**, 37996-41-1; **10c**, 40164-34-9; **11a**, 56258-87-8; **11b**, 62067-15-6; **12a**, 281-15-2; **12b**, 50436-34-5.

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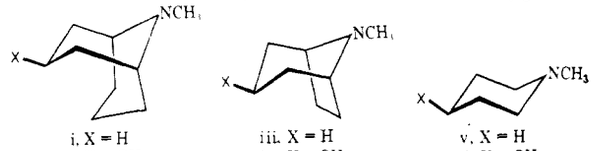

i, X = H; ii, X = OH; iii, X = H; iv, X = OH; v, X = H; vi, X = OH

sytem i. ^{13}C NMR data reveal that on going from i to ii the bridgehead carbon atoms (which are situated in an anti-periplanar arrangement to the 3-*exo*-hydroxy group) experience a *downfield* shift of 1.6 ppm; for the corresponding quaternary methochlorides a downfield shift of 1.3 ppm was observed.[6] In contrast with the above findings are the data for the transformation of iii to iv and the conversion of v to vi for which the analogous carbons show shifts of −1.1 and −3.0 ppm, respectively.[7]
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An Unusual Magnetic Equivalence in the Proton Magnetic Resonance of Dialkylbenzamides

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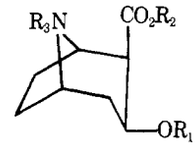
N-Benzoylnorecgonine methyl ester, *N*-benzoylpiperidine, and *N,N*-diethylbenzamide exhibit one set of ^1H NMR signals for aromatic protons whereas cocaine and seven other benzoate esters, acetophenone, α,α,α-trimethylacetophenone, α,α,α-trichloroacetophenone, benzamide, and *N*-ethylbenzamide have two sets separated by ca. δ 0.6. The observed unusual magnetic equivalence of the first three compounds is attributed to the steric interaction of the dialkylamine and the phenyl group with the resultant loss of coplanarity between the phenyl and carbonyl functional groups.

During the course of our investigations on the photochemical behavior of cocaine (I),[1] its photoproducts,[2] and related compounds,[3] the aromatic protons of cocaine were observed to occur as two groups of multiplets in the ^1H NMR spectrum at δ 7.93 (m, 2 H) and 7.36 (m, 3 H), whereas the aromatic proton resonances of *N*-benzoylnorecgonine methyl ester (II), cocaine's O → N benzoyl migration–demethylation product, appear as a sharp singlet at δ 7.45, Table I. This investigation examines the reasons for the surprising proton



I, R_1 = COPh; R_2 = CH_3; R_3 = CH_3
II, R_1 = H; R_2 = CH_3; R_3 = COPh
III, R_1 = COPh; R_2 = CH_3; R_3 = H
IV, R_1 = COPh; R_2 = H; R_3 = CH_3

Table I. ^1H NMR Chemical Shifts of Aromatic Protons of Cocaine and Related Compounds[a]

No.	Compd	Chemical shifts of aromatic protons, δ
I		7.93 (m, 2 H, *o*), 7.36 (m, 3 H, *m,p*)
II		7.45 (s, 5 H)
III		7.96 (m, 2 H, *o*), 7.30 (m, 3 H, *m,p*)
IV		7.90 (m, 2 H, *o*), 7.36 (m, 3 H, *m,p*)
V	Cyclohexyl benzoate	8.03 (m, 2 H, *o*), 7.40 (m, 3 H, *m,p*)
VI	*N*-Methyl-3-piperdinyl benzoate	8.03 (m, 2 H, *o*), 7.40 (m, 3 H, *m,p*)
VII	*N*-Methyl-4-piperdinyl benzoate	8.03 (m, 2 H, *o*), 7.40 (m, 3 H, *m,p*)
VIII	Methyl benzoate	8.00 (m, 2 H, *o*), 7.40 (m, 3 H, *m,p*)
IX	*N*-Benzoylpiperidine	7.30 (s, 5 H)
X	α,α,α-Trimethylacetophenone	7.71 (m, 2 H, *o*), 7.33 (m, 3 H, *m,p*)
XI	α,α,α-Trichloroacetophenone	8.20 (m, 2 H, *o*), 7.50 (m, 3 H, *m,p*)
XII	Acetophenone	7.85 (m, 2 H, *o*), 7.40 (m, 3 H, *m,p*)
XIII	*N,N*-Diethylbenzamide	7.30 (s, 5 H)
XIV	*N*-Ethylbenzamide	7.80 (m, 2 H, *o*), 7.26 (m, 3 H, *m,p*)
XV	Benzamide	8.00 (m, 2 H, *o*), 7.50 (m, 3 H, *m,p*)
XVI	Atropine	7.20 (s, 5 H)

[a] All spectra were recorded in carbon tetrachloride, and the temperature of the A-60 NMR probe was 36 °C.

magnetic equivalence of II and complements earlier studies on the ^1H NMR signal nonequivalence of *N*-alkyl groups in relation to ortho, meta, and para substituents on the phenyl ring.[4-6] The dual set of resonances for the aromatic protons is associated with the direct linkage of the carbonyl group with the phenyl ring. In the model compound atropine (XVI) where the carbonyl group and the phenyl ring are not conjugated, all the aromatic protons appear as a singlet at δ 7.20.

Under ordinary circumstances, carbonyl substituents on aromatic rings cause the ortho protons to be shifted further downfield in the ^1H NMR spectra than the meta and para ones.[7] There is excellent deuterium labeling work which demonstrates this in an unambiguous fashion.[7] Consequently, the proton resonance of I in the downfield shift position from "normal" aromatic proton resonances is caused by the ortho aromatic protons of the phenyl ring which are in an unusual magnetic environment. The positioning of the ortho proton resonance has been attributed to the magnetic anisotropy of the carbonyl group. Logically then, the aromatic protons of II which appear at δ 7.45 are of the "normal" type with no unusual magnetic effects on the ortho aromatic protons.

For routine benzoyl ester groups, nonequivalence of the aromatic protons is expected,[8] i.e., the ortho protons are differentiated from the meta and para ones. in accord with this, all seven benzoate esters examined, I, III–VIII, exhibit two sets of ^1H NMR signals for their aromatic protons, cf. Table I.

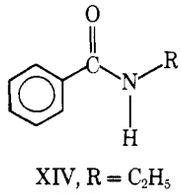
The critical changeover point occurs among the amides. Benzamide and *N*-ethylbenzamide exhibit two sets of ^1H NMR proton signals at δ 8.0 and 7.4 as do the benzoate esters, whereas *N,N*-diethylbenzamide has one set of aromatic proton signals at δ 7.30. The latter observation focuses attention on the *N*-ethylbenzamide and *N,N*-diethylbenzamide model compounds because these are the borderline set of compounds for the observed ^1H NMR phenomenon. The ^1H NMR spectrum of *N*-benzoylnorecgonine methyl ester (II), one of the two compounds responsible for causing the investigation, has one set of aromatic proton signals in agreement with that of *N,N*-diethylbenzamide and *N*-benzoylpiperidine (IX).

Though benzamides show some tendency for cluster formation at higher concentrations, the observations recorded herein are not due to this phenomenon. First, the ^1H NMR spectra of *N*-ethylbenzamide and *N,N*-diethylbenzamide were obtained at room temperature in concentrations of 1, 1×10^{-1}, 5×10^{-2}, 1×10^{-2}, 5×10^{-3}, and 2×10^{-3} M in carbon tetrachloride to study the effect of solute concentration in relation to cluster formation. *N,N*-Diethylbenzamide gives an aromatic proton singlet at δ 7.30 at all concentrations while *N*-ethylbenzamide shows two sets of signals at δ 7.80 and 7.26 in a 1 M solution whereas at lower concentrations (1×10^{-1}, 5×10^{-2}, 1×10^{-2}, 5×10^{-3} M) the signals appear at δ 7.63 and 7.33. Second, in polar solvents where cluster formation is less likely, the room temperature ^1H NMR spectra of *N*-ethylbenzamide in deuterated acetone and dimethyl sulfoxide exhibit two sets of aromatic proton signals (δ 7.70, 7.30 and 7.83, 7.40, respectively) and *N,N*-diethylbenzamide a singlet (δ 7.30 in both).

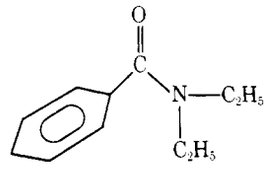
The magnetic equivalence of aromatic protons of the more bulky amides is not due to simple steric requirements alone. α,α,α-Trimethylacetophenone was synthesized and its ^1H NMR spectrum observed in order to evaluate the steric hindrance effect of a large substitution on one side of the carbonyl. Interestingly, the *tert*-butyl ketone also had two aromatic ^1H NMR proton signals centered at δ 7.71 and 7.33 similar to the *N*-ethylbenzamide and the parent compound, acetophenone. Thus the steric interaction of the bulky *tert*-butyl group did not change the nonequivalence of the aromatic protons. To demonstrate that this observation was not caused by a fortuitous canceling of factors originating in the electron-releasing property of the methyl groups, the sterically hindered α,α,α-trichloroacetophenone was synthesized; and it, too, exhibited two sets of aromatic proton signals in the ^1H NMR spectrum albeit with shifts downfield.

By using a combination of resonance and steric arguments, an explanation consistent with the data can be obtained. For optimum resonance interaction of benzamide, the phenyl ring, the carbonyl, and the disubstituted amide should be coplanar. There is a cross conjugation of the amide with the carbonyl group which is absent or minimized in benzoate esters and phenyl ketones. Whereas the barriers to rotation about normal carbon–carbon and carbon–nitrogen double bonds are in excess of 40 kcal/mol,[9] the carbon–nitrogen bond in amides possesses sufficient double bond character to provide a remarkable barrier to rotation, i.e., 10–25 kcal/mol.

The coplanarity which gives rise to the dual set of aromatic proton resonances can be achieved readily in benzamide (XV) and *N*-ethylbenzamide (XIV), but for *N,N*-diethylbenzamide (XIII), II, and IX, the nitrogen–carbonyl resonance is maintained but the phenyl ring is forced out of conjugation with the carbonyl group. The effect of the lack of the coplanarity between the phenyl ring and amide carbonyl is the equivalence of the aromatic protons as well as the differentiation of the two sets of methylene protons of the *N*-ethyl groups.[10]



XIV, R = C_2H_5
XV, R = H



XIII

If the explanation is correct, the observation that α,α,α-trimethylacetophenone and α,α,α-trichloroacetophenone exhibit two sets of aromatic protons whereas *N,N*-diethylbenzamide gives one must again be reviewed. The rationalization for the observed results is that the second alkyl group of *N,N*-diethylbenzamide more directly sterically interferes with the phenyl ring due to the partial double bond character of the C–N bond than does the non-cross-conjugated, more freely rotating alkyl group of α,α,α-trimethylacetophenone. Furthermore, the reduction in resonance between the aromatic ring and the carbonyl of *N,N*-diethylbenzamide presumably is compensated for by an increase in the double bond character of the nitrogen carbonyl linkage.[5a]

Experimental Section

The melting points were obtained on a Fisher-Johns melting point apparatus. The infrared spectra were taken on a Beckman Model IR-12 spectrophotometer. The proton magnetic resonance spectra were taken at room temperature on a Varian Associates A-60 instrument using tetramethylsilane as an internal standard. The chemical shifts of various compounds are given in δ units.

Cocaine hydrochloride was purchased from Merck and Co., Inc., St. Louis, Mo. Atropine, trimethylacetyl chloride, piperidine, 1-methyl-3-piperidinol, and 1-methyl-4-piperidinol were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis. Trichloroacetyl chloride was purchased from Eastman Kodak Co., Rochester, N.Y. All alcohols, acid chlorides, and benzoyl chloride were freshly distilled before use.

Cocaine (I). Free cocaine was obtained by neutralizing cocaine hydrochloride with 10% NH_4OH solution followed by extraction with ether and recrystallization from ethanol: mp 98 °C (lit.[11] mp 98 °C); NMR (CCl_4) δ 7.93 (m, 2 H, C_6H_5), 7.36 (m, 3 H, C_6H_5), 5.10 (m, 1 H, $-CHOCOC_6H_5$), 3.60 (s, 3 H, $-COOCH_3$), 3.50 (1 H, C_1 H), 3.20 (1 H, C_5 H), 2.90 (1 H, C_2 H), 2.20 (NCH_3), and 1.70–2.10 (m, ring CH_2 protons).

***N*-Benzoylnorecgonine Methyl Ester (II), Norcocaine (III), and *O*-Benzoylecgonine (IV).** Norcocaine was obtained by oxidation of cocaine by potassium permanganate at controlled pH 2: mp 78–80 °C (lit.[12] mp 80–82 °C); NMR (CCl_4) δ 7.96 (m, 2 H of C_6H_5), 7.30 (m, 3 H of C_6H_5), 5.00 (m, 1 H, CHOCOPh), 3.60 (s, 3 H, OCH_3), 3.10 (s, 1 H, $CHCO_2CH_3$), and 1.60–2.30 (m, 8 H, ring CH_2 and CH). *O*-Benzoylecgonine (IV) was also obtained in the above reaction:[2] mp 196–197 °C (lit.[13] mp 197–201 °C); NMR (CCl_4) δ 7.90 (m, 2 H of C_6H_5), 7.36 (m, 3 H of C_6H_5), 5.13 (m, 1 H, CHOCOPh), 3.15 (m, 1 H, $CHCO_2H$), 2.40 (s, 3 H, NCH_3), and 1.80–2.20 (m, 8 H, ring CH_2 and CH protons). *N*-Benzoylnorecgonine methyl ester (II) was obtained by $KMnO_4$ oxidation of cocaine in basic medium:[14] mp 141 °C; NMR (CCl_4) δ 7.45 (s, 5 H, aromatic), 3.6 (s, 3 H, OCH_3).

Cyclohexyl Benzoate (V). Equimolar quantities of benzoyl chloride and cyclohexanol in dry benzene were stirred vigorously for 2 h. The reaction mixture was extracted with sodium carbonate solution. The organic layer was washed with water and dried over anhydrous sodium sulfate. A yellowish liquid was obtained after removal of benzene. The cyclohexyl benzoate was collected at 192 °C (61 mm) [lit.[15] bp 192–193 °C (61 mm)]; IR (CCl_4) 1705 cm^{-1} (C=O); NMR (CCl_4) δ 8.03 (m, 2 H, C_6H_5), 7.40 (m, 3 H, C_6H_5), 5.00 (m, 1 H, $CHOCOC_6H_5$), and 1.6 (br m, 10 H, ring CH_2).

***N*-Methyl-3-piperidinyl Benzoate (VI).** This compound was prepared by stirring equimolar quantities of benzoyl chloride and *N*-methyl-3-piperidinol in dry benzene at room temperature for 2 h and worked up as usual. The pure *N*-methyl-3-piperidinyl benzoate was collected at 94–95 °C (0.05 mm) [lit.[16] 94–97 °C (0.05 mm)]: IR (CCl_4) 1710 cm^{-1} (C=O); NMR (CCl_4) δ 8.03 (m, 2 H, C_6H_5), 7.40 (m, 3 H, C_6H_5), 5.00 (m, 1 H, $-CHOCOC_6H_5$), 2.25 (s, 3 H, NCH_3), and 1.70–3.00 (m, 8 H, ring CH_2).

***N*-Methyl-4-piperidinyl Benzoate (VII).** Following the procedure of VI, *N*-methyl-4-piperidinyl benzoate was prepared and distilled at 161–163 °C (10 mm). The melting point of *N*-methyl-4-piperidinyl benzoate hydrochloride was 200 °C (lit.[17] 219–220 °C): IR (CCl_4) 1710 cm^{-1} (C=O); NMR (CCl_4) δ 8.03 (m, 2 H, C_6H_5), 7.40 (m, 3 H, C_6H_5), 5.00 (m, 1 H, $-CHOCOC_6H_5$), 2.25 (s, 3 H, NCH_3), and 1.70–2.90 (m, 8 H, ring CH_2).

***N*-Benzoylpiperidine (IX).** A mixture of piperidine and benzoyl chloride in dry benzene in a 2:1 molar ratio was stirred for 2 h. The workup of reaction mixture yielded *N*-benzoylpiperidine: bp 195 °C (25 mm) [lit.[18] 195 °C (25 mm)]; NMR (CCl_4) δ 7.30 (s, 5 H, C_6H_5), 3.40 (m, 4 H, $-CH_2NCH_2-$), and 1.60 (m, 6 H, ring CH_2).

α,α,α-Trimethylacetophenone (X). α,α,α-Trimethylacetophenone was prepared by Friedel–Crafts reaction using trimethylacetyl chloride, dry benzene, anhydrous aluminum chloride as reagents: bp 104 °C (13 mm) [lit.[19] bp 103–104 °C (13 mm)]; IR (CCl_4) 1675 cm^{-1} (C=O); NMR (CCl_4) δ 7.71 (m, 3 H, C_6H_5), 7.33 (m, 2 H, C_6H_5), and 1.30 (s, 9 H, CH_3).

α,α,α-Trichloroacetophenone (XI). This was also prepared by Friedel–Crafts reaction using trichloroacetyl chloride, dry benzene, and anhydrous aluminum chloride as reagents. α,α,α-Trichloroacetophenone was distilled as a colorless liquid: bp 145 °C (25 mm) [lit.[20] 145 °C (25 mm)]; IR (CCl_4) 1715 cm^{-1} (C=O); NMR (CCl_4) δ 8.20 (m, 2 H, C_6H_5) and 7.50 (m, 3 H, C_6H_5).

***N,N*-Diethylbenzamide (XIII).** A mixture of diethylamine and benzoyl chloride in molar ratio of 2:1 in dry benzene was stirred for 1 h and worked up to yield *N,N*-diethylbenzamide: bp 280 °C (lit.[21] bp 280–282 °C); NMR (CCl_4) δ 7.30 (s, 5 H, C_6H_5), 3.30 (q, 2 H, $-CH_2CH_3$), and 1.10 (t, 3 H, $-CH_2CH_3$).

***N*-Ethylbenzamide (XIV).** This was prepared by passing dry ethylamine into the ethereal solution of benzoyl chloride. After saturation and standing for 2.5 h, the ether layer was extracted with sodium carbonate solution, washed with water, and dried over anhydrous sodium sulfate. Removal of ether resulted in a white solid which was recrystallized from alcohol: mp 60 °C (lit.[21] mp 68–69 °C); NMR (CCl_4) δ 7.80 (m, 2 H, C_6H_5), 7.26 (m, 3 H, C_6H_5), 3.30 (q, 2 H, $-CH_2CH_3$), and 1.13 (t, 3 H, $-CH_2CH_3$).

Atropine (XVI). Atropine: NMR (CCl_4) δ 7.20 (s, 5 H, aromatic), 4.90 (t, J = 5 Hz, 1 H, C_3 H), 4.00 (m, 1 H, $COCHPhCH_2OH$), 3.63 (m, 2 H, CH_2OH), 2.80–2.90 (br, 2 H, C_5 H and C_1 H), 2.10 (s, 3 H, NCH_3), and 1.30–2.15 (br, s, 9 H, C_4, C_6, C_7 CH_2 protons, OH).

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Registry No.—I, 50-36-2; I HCl, 53-21-4; II, 17366-44-8; III, 18717-72-1; IV, 519-09-5; V, 2412-73-9; VI, 16597-31-2; VII, 16597-30-1; VII HCl, 40378-58-3; VIII, 93-58-3; IX, 776-75-0; X, 938-16-9; XI, 2902-69-4; XII, 98-86-2; XIII, 1696-17-9; XIV, 614-17-5; XV, 55-21-0; XVI, 51-55-8; benzoyl chloride, 98-88-4; cyclohexanol, 108-93-0; *N*-methyl-3-piperidinol, 3554-74-3; *N*-methyl-4-piperidinol, 106-52-5; piperidine, 110-89-4; trimethylacetyl chloride, 3282-30-2; benzene, 71-43-2; trichloroacetyl chloride, 76-02-8; diethylamine, 109-89-7; ethylamine, 75-04-7.

References and Notes

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