Gas Chrom P (wt./wt.), maintained at 300°. The analytical column was a $^3/_{16}$-in. o.d. copper column containing 5% squalane on acid-washed Chromosorb W maintained at 110°. Both acids gave appreciable amounts of only one peak at 11.4 min. This retention time coincided precisely with that of nonane.

Nuclear Magnetic Resonance Spectra.—These were obtained on a Varian Associates Model A-60 spectrometer. Deuteriowater was used as the solvent because the solubility of the acids in the commonly used deuteriochloroform is too low. The spectrum of hydroxywilfordic acid was made with microplugs supplied by Varian Associates.

Optical Rotation.—In water the optical rotation was $[\alpha]^{24}\text{D}$ +6.98° for wilfordic acid and $[\alpha]^{24}\text{D}$ −24.1° for hydroxywilfordic acid.

Acknowledgment.—The author thanks Mrs. K. S. Warren of the National Institutes of Health for determining the optical rotation of the acids and Mr. Don Hollis of Varian Associates for reviewing the interpretation of the n.m.r. spectra.

Application of Nuclear Magnetic Resonance Spectroscopy to Keto Acid–Pseudoacid Tautomerism

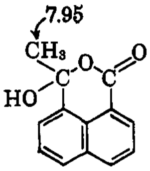
PETER T. LANSBURY AND JOSEPH F. BIERON[1]

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York

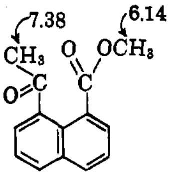
Received July 15, 1963

Infrared[2] and ultraviolet[3] spectroscopy have been frequently used to study the structure as well as equilibrium composition of ring-chain tautomers of *o*-acylbenzoic and *o*-aroylbenzoic acids and their esters. Bonner[4] recently has made a detailed study of the normal and pseudo (ψ) methyl and (−)-menthyl esters of *o*-benzoylbenzoic acid (which is mainly in the open form[2a]), using not only infrared and ultraviolet spectroscopy for determining structure and detecting mixtures, but optical rotatory dispersion and thin layer chromatography as well. In connection with another problem, we have examined the nuclear magnetic resonance (n.m.r.) spectra of 8-acetyl-1-naphthoic acid and its normal and ψ-methyl esters, as well as the methyl *o*-benzoylbenzoates. This technique is extremely rapid and straightforward and may have general utility in the qualitative and quantitative analysis of normal and pseudoesters, particularly methyl esters, since unsplit methyl proton signals are easily seen and appear at different positions in the spectra, depending on which tautomer is present.

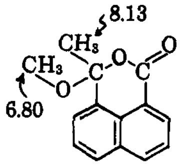
8-Acetyl-1-naphthoic acid (I) reportedly[5] does not give carbonyl derivatives, and its infrared spectrum further suggests that it exists as the pseudoacid. We have confirmed this by comparing the n.m.r. spectrum with the normal (II) and ψ- (III) methyl esters, which were prepared by treating I with diazomethane and acidified methanol, respectively. The chemical shifts (τ) of the various methyl protons are indicated. The methyl signals in II are typical[6] for methyl aryl ketones and methyl benzoates, whereas the 6.80-τ signal in III is in the expected region for methyl ethers.[6] The 8.13-τ signal in III corresponds closely with the *single* methyl peak in I, thus confirming the ψ-acid character of I. Ultraviolet spectroscopy also shows that I exists in the ψ-acid form, as Table I indicates.



I



II



III

TABLE I

Compound	λ_{max} mμ	log ε
I	310	3.91
II	296	3.95
III	310	3.95

The quantitative analysis of mixtures of normal and ψ-esters can be accomplished readily by n.m.r. spectroscopy, using the peak areas of the individual methyl groups to calculate the ratio of the tautomers present. For example, a synthetic mixture containing 40.6% of II and 59.4% of III gave 41% II and 59% III by electronic integration on the A-60 spectrometer. Also, a synthetic mixture containing 52.7% of methyl *o*-benzoylbenzoate[7] (τ_{CH_3} 6.53) and 47.3% of methyl ψ-*o*-benzoylbenzoate[7] (τ_{CH_3} 6.82) contained 52% of the former and 48% of the latter by integration as above.

Experimental[8]

Pseudo Methyl Ester of 8-Acetyl-1-naphthoic Acid (III).—A solution of 5.6 g. of 8-acetyl-1-naphthoic acid[5] in 60 ml. of methanol containing a few drops of sulfuric acid was heated for 2 hr. on a steam bath. The reaction mixture was poured into water and extracted with ether. The ether was washed with 10% sodium hydroxide solution, water, and then dried over sodium sulfate. Evaporation of the ether, followed by recrystallization of the residue from methanol–water gave a quantitative yield (6.0 g.) of III, m.p. 102.5–103°, whose infrared spectrum (Nujol mull) showed a single carbonyl band at 1715 cm.$^{-1}$ (lactone).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 74.2; H, 5.2.

Normal Methyl Ester of 8-Acetyl-1-naphthoic Acid (II).—An excess of ethereal diazomethane was added to 4.0 g. of 8-acetyl-1-naphthoic acid in ether, whereupon gas evolution began immediately. After 3 hr., the yellow solution was filtered and evaporated under nitrogen. The yellow crystalline residue was recrystallized from petroleum ether (b.p. 60–90°) to give II in quantitative yield, m.p. 92–93°. This ester showed infrared carbonyl bands (in Nujol) at 1660 (ketone) and 1725 cm.$^{-1}$ (ester).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.6; H, 5.2.

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[1] National Science Foundation predoctoral Fellow, 1962–1964.

[2] (a) M. Renson, *Bull. soc. chim. Belges*, **70**, 77 (1961); (b) D. D. Wheeler, D. C. Young, and D. S. Earley, *J. Org. Chem.*, **22**, 547 (1957); (c) P. R. Jones and S. L. Congdon, *J. Am. Chem. Soc.*, **81**, 4291 (1959).

[3] M. S. Newman and C. W. Muth, *ibid.*, **73**, 4627 (1951).

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[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 54.

[7] We thank Professor W. A. Bonner for samples of these compounds.

[8] Melting points were taken in a "Mel-temp" capillary tube melting point apparatus and are uncorrected. Elemental analyses were performed by Dr. Alfred Bernhardt, Mülheim, Germany.

Spectroscopic Measurements.—Ultraviolet spectra of compounds I–III were measured in ethanol, using a Beckman DK-2 recording spectrometer.

Nuclear magnetic resonanece spectra were taken in a Varian A-60 spectrometer.[9] Both sets of methyl esters (see discussion) were run in carbon tetrachloride solution, whereas acid I was studied in chloroform-*d*.

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[9] We thank the Buffalo Medical Foundation for the use of their n.m.r. facilities.

The Ultraviolet and Infrared Spectra of Some *o*-Nitroamides[1a]

Lech Skulski[1b]

Department of Chemistry, University of California, Berkeley 4, California

Received May 6, 1963

The existence of intramolecular hydrogen bonding in the molecule of *o*-nitroacetanilide has been supported by cryoscopic and wet melting point measurements,[2] dipole moments,[3] polarographic,[4] infrared,[5] and ultraviolet[6] studies. This evidence also is confirmed by the relatively greater volatility[4] and solubility of this compound in naphthalene[2] and cyclohexane, when compared with the *meta* and *para* isomers.

The new measurements of the ultraviolet absorption of *o*-nitroacetanilide (I) and its N-methyl derivative (II) carried out in solutions of cyclohexane and in mixtures of cyclohexane with methanol, ethanol, and pyridine (*cf.*, for example, Fig. 1)[7] reveal profound changes of the acetanilide spectra with solvents, while those of the N-methyl derivative are only slightly affected. Common isobestic points in the curves for I would indicate an equilibrium of two absorbing species existing in solutions of I. Dilute cyclohexane solution of I contains internally H-bonded coplanar molecules. The amount of internal H-bonding is reduced by the addition of increasing amounts of an alcohol or pyridine to the dilute solution of internally bonded compound in an inert (hydrocarbon) solvent which gives rise to solvated noncoplanar species, and the spectra become similar to those of the N-methyl derivative.

Similarly, the ultraviolet spectra of 2-nitro-*p*-acetotoluidide (III), 1-nitro-2-acetonaphthalide (V), and their N-methyl derivatives (IV and VI), respectively, show that similar equilibria exist also in solutions of III and V, as well as in solutions of 2,4-dimethyl-6-nitroacetanilide (VII) (Fig. 2–5).

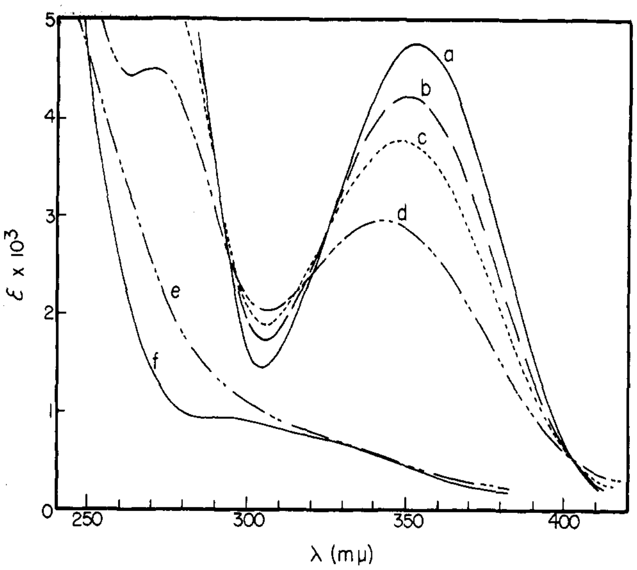

Fig. 1.—Ultraviolet spectra of *o*-nitroacetanilide (I, curves a–d) and N-methyl-*o*-nitroacetanilide (II, curves e, f), 0.0002 mole/l. in four solvents: a, f, cyclohexane; b, 92% cyclohexane–8% ethanol; c, 80% cyclohexane–20% ethanol; d, e, 20% cyclohexane–80% ethanol (by volume).

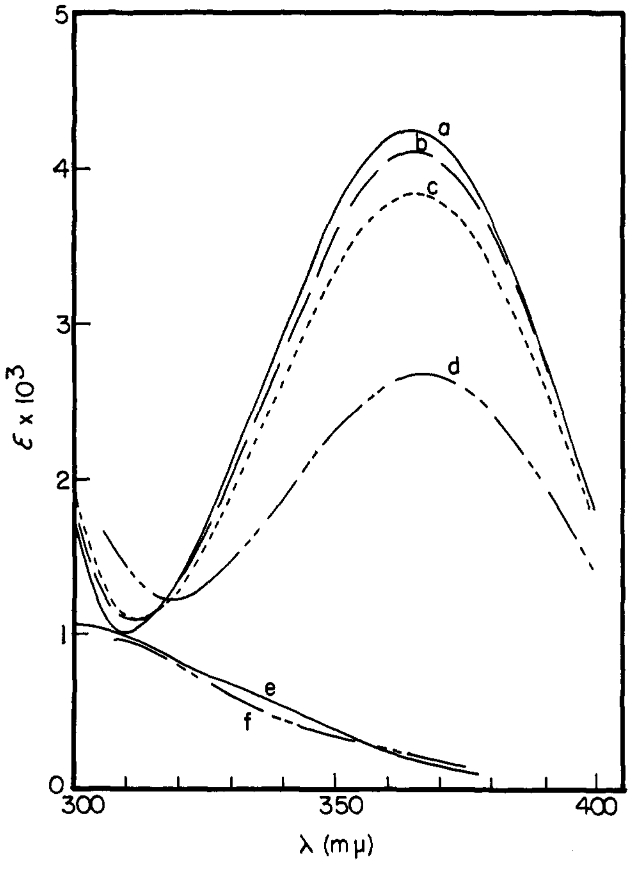

Fig. 2.—Ultraviolet spectra of 2-nitro-*p*-acetotoluidide (III, curves a–d) and N-methyl-2-nitro-*p*-acetotoluidide (IV, curves e, f), 0.0002 mole/l. in four solvents: a, e, cyclohexane; b, 96% cyclohexane–4% pyridine; c, 90% cyclohexane–10% pyridine; d, f, 20% cyclohexane–80% pyridine (by volume).

The existence of internal hydrogen bonding for III and V, and the lack of chelate structure in the molecule of VII, due to steric crowding, was suggested by Chaplin and Hunter.[2] Yet, according to Forbes, *et al.*,[5] infrared spectra seem to indicate that neither V nor VII is intramolecularly hydrogen bonded in (chloroform)

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[1] (a) This paper was presented at the International Symposium on Nitro-compounds, Warsaw (Poland), September 18, 1963. (b) Postdoctoral Fellow, 1962–1963; on leave of absence from the Institute of Technology (Politechnika), Warsaw, Poland; appointment supported by the Ford Foundation Polish Exchange Program, administered by the Institute of International Education, N. Y.

[2] H. O. Chaplin and L. Hunter, *J. Chem. Soc.*, 375 (1938).

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[7] The ultraviolet absorption spectra were determined with a Cary Model 14 recording spectrophotometer using 1-cm. silica cells and 0.0002 mole/l. solutions. Solutions were prepared by transferring 5.00 ml. of 0.001 mole/l. solutions in cyclohexane into 25.00-cc. volumetric flasks, adding an appropriate amount of methanol, ethanol, or pyridine (by volume), and by filling the flasks with cyclohexane.