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*.

---

[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).

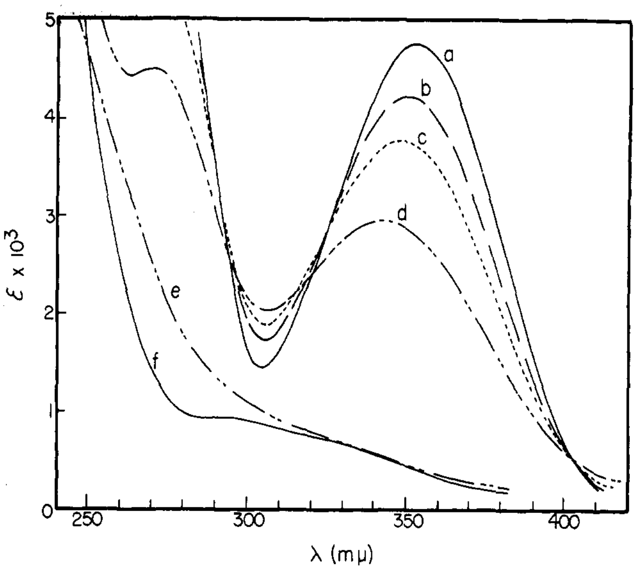


Fig. 1.—Ultraviolet spectra of *o*-nitroacetanilide (I, curves a–d) and N-methyl-*o*-nitroacetanilide (II, curves e, f), 0.0002 mole/l. in four solvents: a, f, cyclohexane; b, 92% cyclohexane–8% ethanol; c, 80% cyclohexane–20% ethanol; d, e, 20% cyclohexane–80% ethanol (by volume).

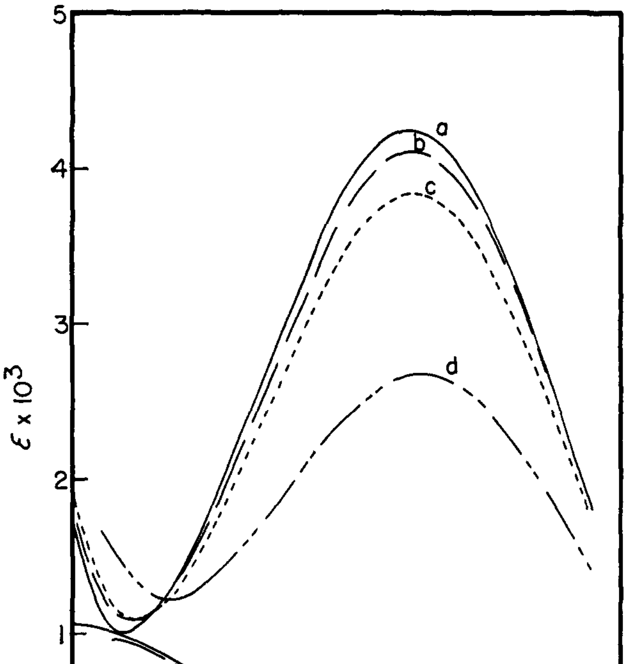


Fig. 2.—Ultraviolet spectra of 2-nitro-*p*-acetotoluidide (III, curves a–d) and N-methyl-2-nitro-*p*-acetotoluidide (IV, curves e, f), 0.0002 mole/l. in four solvents: a, e, cyclohexane; b, 96% cyclohexane–4% pyridine; c, 90% cyclohexane–10% pyridine; d, f, 20% cyclohexane–80% pyridine (by volume).

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)

---

(1) (a) This paper was presented at the International Symposium on Nitrocompounds, 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).

(3) A. E. Lutskii and B. P. Kondratenko, *Zh. Obshch. Khim.*, **29**, 2077 (1959).

(4) M. E. Runner and E. C. Wagner, *J. Am. Chem. Soc.*, **74**, 2529 (1952).

(5) E. J. Forbes, K. J. Morgan, and J. Newton, *J. Chem. Soc.*, 835 (1963).

(6) H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 5133 (1954); A. E. Lutskii, *et al.*, *Zh. Obshch. Khim.*, **30**, 3782 (1960).

(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.

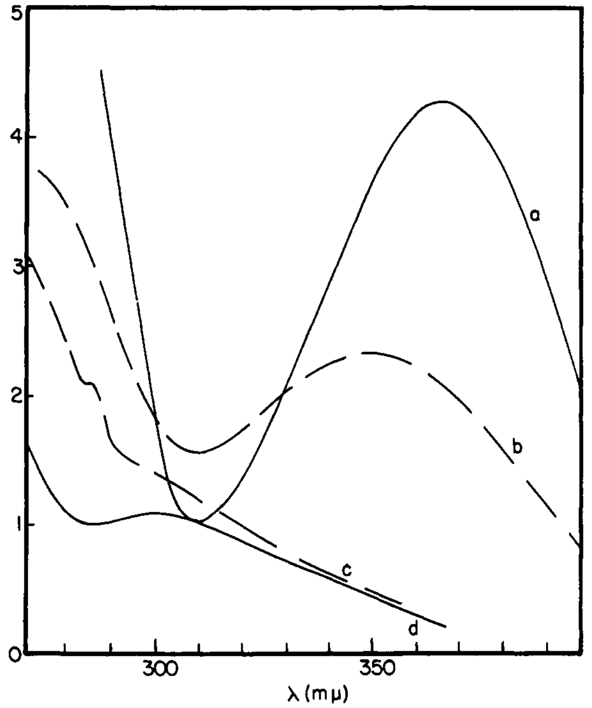


Fig. 3.—Ultraviolet spectra of 2-nitro-*p*-acetotoluidide (III, curves a, b) and N-methyl-2-nitro-*p*-acetotoluidide (IV, curves c, d), 0.0002 mole/l. in two solvents: a, d, cyclohexane; b, c, 20% cyclohexane–80% methanol (by volume).

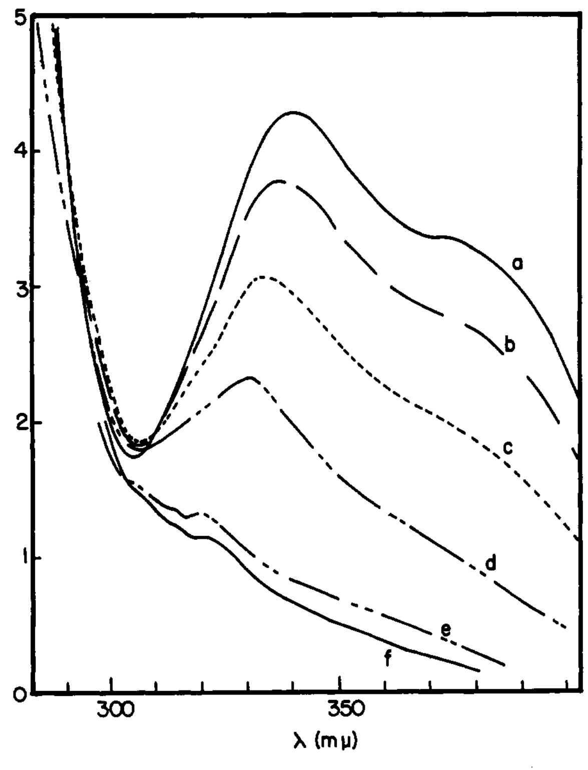


Fig. 4.—Ultraviolet spectra of 1-nitro-2-acetonaphthalide (V, curves a–d) and N-methyl-1-nitro-2-acetonaphthalide (VI, curves e, f), 0.0002 mole/l. in four solvents: a, f, cyclohexane; b, 99% cyclohexane–1% methanol; c, 96% cyclohexane–4% methanol; d, e, 20% cyclohexane–80% methanol (by volume).

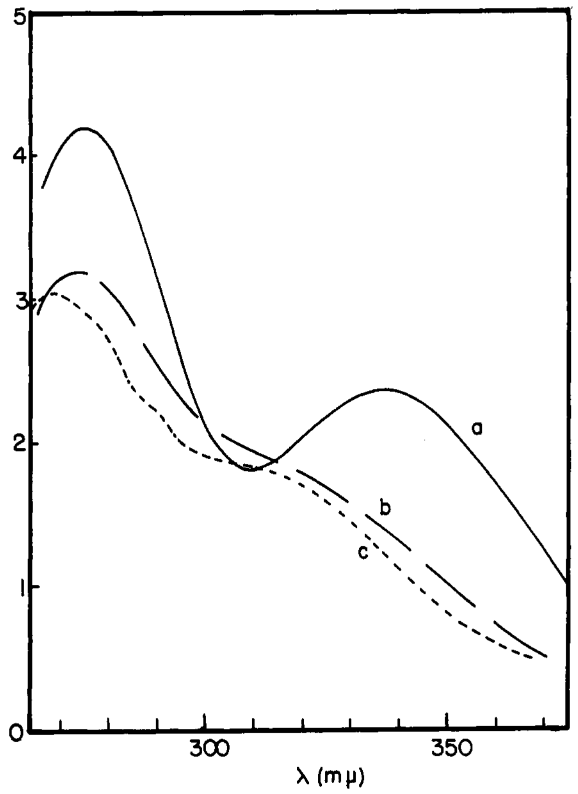
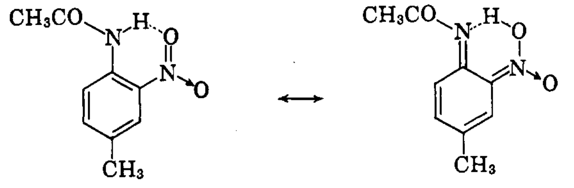


Fig. 5.—Ultraviolet spectra of 2,4-dimethyl-6-nitroacetanilide (VII), 0.0002 mole/l. in three solvents: a, cyclohexane; b, 20% aqueous methanol (by volume); c, methanol.

solutions. Ultraviolet spectra presented in this paper seem, nevertheless, to point out the existence of fairly strong internal hydrogen bonding in the cyclohexane solutions of I and III, less strong in V, and weak in the molecule of VII.

It is known[8,9] that 2-nitro-*p*-acetotoluidide (III) may exist in the two different crystalline forms: stable white (m.p. 95°) and metastable yellow (m.p. 93.5°). These two forms have the same ultraviolet solution spectra, but their ultraviolet and infrared solid spectra differ considerably (Fig. 6).[10] It also was established that the yellow form of III by prolonged grinding or mixing with potassium bromide may be partially or completely converted into the white form[11] (Fig. 6). These facts seem to point out that the yellow form of III (closely corresponding to the only existing yellow form of I) exists in the solid state as strongly internally hydrogen-bonded species.[12]



---

(8) L. Gattermann, *Ber.*, **23**, 1733 (1890).

(9) K. Schaum, *Ann.*, **462**, 194 (1928); the existence of the third dark yellow form (which is quickly transformed into the pale yellow one) was reported here.

(10) The preliminary studies have shown a similarity between the ultraviolet spectra of yellow form of III in solid state and in cyclohexane solution. There also is a resemblance between solid spectra of IV and the white form of III. These measurements were carried out on suspensions of the solid compounds in Nujol and in a highly viscous perfluorocarbon.

(11) For infrared studies on the influence of the time of mixing the samples with KBr, Wig-L-Bug amalgamator (Crescent Dental Mfg. Co., Chicago, Ill., Model 5A) was used, and mixing time was changed within the limits of 30 to 300 sec. After 5 min. of mixing the yellow form of III with KBr, the infrared spectrum was completely identical with the spectrum of the white form. No changes due to mixing with KBr were observed in the case of I, V, VII, and several other *o*-nitroacetanilides. Infrared spectra were determined on a Perkin-Elmer Model 237 instrument.

(12) The closure of the chelate ring very likely strongly stabilizes the quinoid structure.

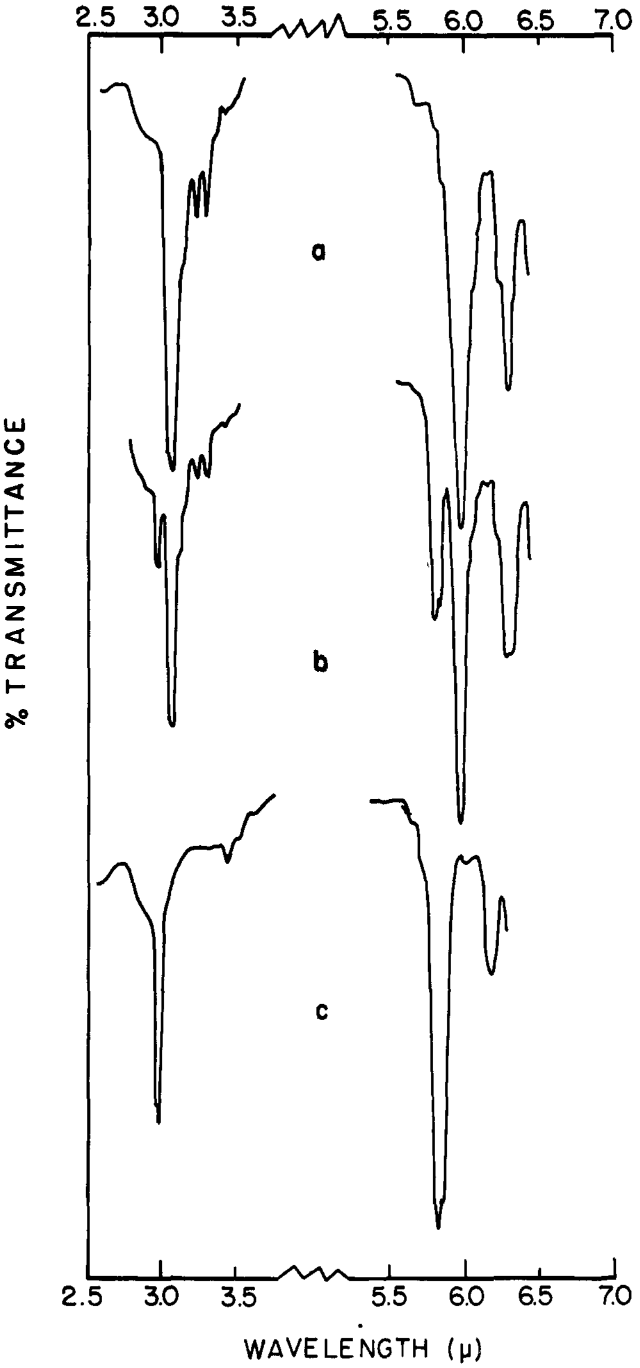


Fig. 6.—Infrared spectra of solid 2-nitro-p-acetotoluidide (III) pressed in KBr[11]: a, white form shaken with KBr for 30 sec.; b, yellow form shaken with KBr for 120 sec.; c, yellow form shaken with KBr for 30 sec.

Contrary to this, the white form of III possesses probably the true amide structure stabilized by intermolecular hydrogen bondings. Infrared spectra show that the carbonyl group in the white form is hydrogen bonded, in the yellow form is free. This presents clear evidence for assignment of inter- and intramolecularly hydrogen-bonded structures to the white and yellow crystal forms of III.

Further systematic studies of a number of 2-nitroacetanilides substituted in the 4-position are now in progress. The results of these studies will be published later.

Experimental[13]

o-Nitroacetanilide (I), 1-nitro-2-acetonaphthalide (V), and 2,4-dimethyl-6-nitroacetanilide (VII) are commercially available materials which were recrystallized before use. 2-Nitro-*p*-acetotoluidide (III) was obtained by acetylation of commercially available free amine with acetic anhydride. The low melting yellow form (m.p. 93.5–94°) and the high melting white form (m.p. 95–96°) have been obtained according to Gattermann.[8]

N-Methyl derivatives II, IV, and VI or I, III, and V, respectively, were prepared with a good yield by the method developed by Pachter and Kloetzel.[14] Their structure was confirmed by their melting points, fairly close to those described in the literature, and by the results of microanalyses[15] and infrared spectra.

Anal. Calcd. for $C_9H_{10}N_2O_3$ (II), m.p. 70–71.5° (lit.[16] m.p. 70°): C, 55.67; H, 5.19; N, 14.43. Found: C, 55.67; H, 5.10; N, 14.55.

Calcd. for $C_{10}H_{12}N_2O_3$ (IV), m.p. 65–66° (lit.[17] m.p. 64°): C, 57.68; H, 5.81; N, 13.46. Found: C, 57.88; H, 5.83; N, 13.37.

Calcd. for $C_{13}H_{12}N_2O_3$ (VI), m.p. 114–115° (lit.[18] m.p. 112–113°): C, 63.92; H, 4.96; N, 11.47. Found: C, 64.16; H, 4.98; N, 11.55.

Acknowledgment.—The author wishes to thank Professor Melvin Calvin for many helpful discussions during the course of this work, and to acknowledge the valuable comments of the referees.

---

(13) All melting points are uncorrected.

(14) I. J. Pachter and M. C. Kloetzel, *J. Am. Chem. Soc.*, **74**, 1321 (1952).

(15) All microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California.

(16) M. A. Philips, *J. Chem. Soc.*, 2820 (1029).

(17) St. Niementowski, *Ber.*, **20**, 1874 (1887).

(18) R. Meldola and J. H. Lane, *J. Chem. Soc.*, **85**, 1592 (1906).

The Removal of the 1-Methoxyl Group from 1,2,9,10-Tetramethoxydibenz[*de,g*]quinolin-7-one by Catalytic Hydrogenation

J. Cohen and W. I. Taylor

The Research Department, Ciba Pharmaceutical Company, Division of Ciba Corporation, Summit, New Jersey

Received June 6, 1963

We recently have recognized and proven by synthesis[1] the structures of liriodenine (I) and 1,2,9,10-tetramethoxydibenz[*de,g*]quinolin-7-one (II), the two yellow alkaloids[2] of *Liriodendron tulipifera* L. Since then a number of groups have identified their alkaloids with liriodenine, *viz.*, oxoushinsunine from *L. tulipifera* L.,[3] *Michelia compressa* Maxim.,[4] *M. compressa* Maxim. var. *formosana Kanchira*,[5,6] *M. Alba* DC.,[7] and *Magnolia coco* (Lour.) DC.[8]; and spermatheridine from *Atherosperma moschatum* Labill.[9] Liriodenine has since been prepared from the aporphines, roemerine, or ushinsunine by chromic acid or manganese oxide oxidations,[10,6] and the reverse reaction has been accom-

---

(1) W. I. Taylor, *Tetrahedron*, **14**, 42 (1961); J. Cohen, W. Von Langenthal, and W. I. Taylor, *J. Org. Chem.*, **26**, 4143 (1961).

(2) M. A. Buchanan and E. E. Dickey, *ibid.*, **25**, 1389 (1960).

(3) M. Tomita and H. Furukawa, *J. Pharm. Soc. Japan*, **82**, 1199 (1962).

(4) M. Tomita and H. Furukawa, *ibid.*, **82**, 925 (1962).

(5) T.-H. Yang, *ibid.*, **82**, 794 (1962).

(6) S.-S. Yang, W.-Y. Huang, L. C. Lin, and P.-Y. Yeh, *Chemistry* (Taipei), 144 (1961). In this reference the alkaloid also is called micheline.

(7) T.-H. Yang, *J. Pharm. Soc. Japan*, **82**, 811 (1962).

(8) T.-H. Yang, S. Lu, and C. Hsiao, *ibid.*, **82**, 816 (1962).

(9) I. R. C. Bick, P. S. Clezy, and W. D. Crow, *Australian J. Chem.*, **9**, 111 (1956). Identity was established by direct comparison: I. R. C. Bick; personal communication.