[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Steric Effects in the Ultraviolet Absorption Spectra of Aromatic Nitro Compounds

BY WELDON G. BROWN AND HARRIET REAGAN

With the objective of comparing the steric inhibition of resonance caused by alkyl groups in ortho-substituted aromatic nitro compounds, we have examined the ultraviolet absorption spectra of the mono-nitro derivatives of toluene, cumene, *t*-butylbenzene and mesitylene. The inhibition of nitro-group resonance by ortho-methyl groups has been shown spectroscopically by Sherwood and Calvin[1] and by Remington.[2] It was to be expected that the higher alkyl groups would be more effective than methyl groups in blocking a coplanar configuration of the nitro group and consequently that the characteristic nitro-group absorption band would be progressively weakened as larger groups are introduced.

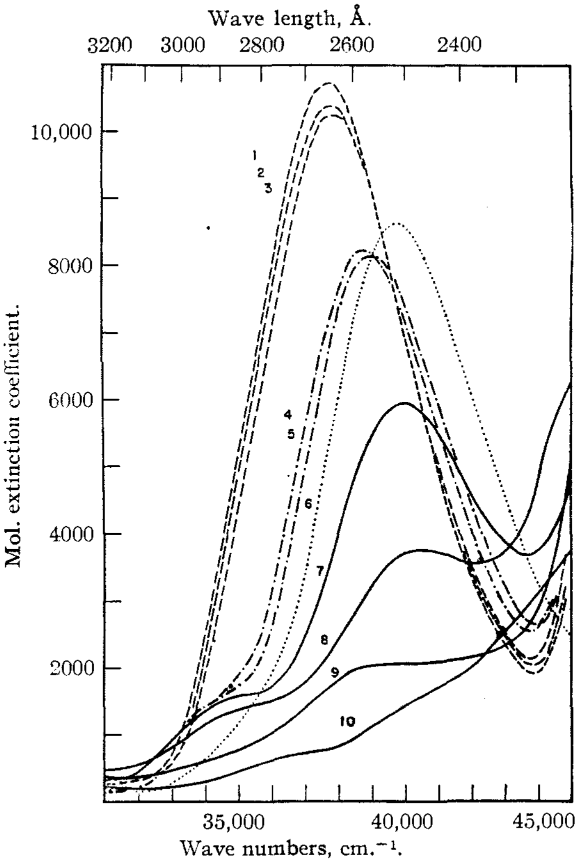

Fig. 1.—1, *p*-Nitro-*t*-butylbenzene; 2, *p*-nitrocumene; 3, *p*-nitrotoluene; 4, *m*-nitro-*t*-butylbenzene; 5, *m*-nitrotoluene; 6, nitrobenzene; 7, *o*-nitrotoluene; 8, *o*-nitrocumene; 9, nitromesitylene; 10, *o*-nitro-*t*-butylbenzene.

To what extent this expectation is borne out may be seen by inspection of the curves in Fig. 1. For the purposes of this study the para-nitro derivatives serve as reference compounds. The spectra of these form a set of closely parallel curves (curves 1–3), in which the maximum, at 2650 Å., increases slightly in the order, according to alkyl groups—methyl, *i*-propyl, *t*-butyl. Likewise the meta-nitro compounds (curves 4, 5; *m*-nitro-*i*-propylbenzene is missing due to our inability to effect the synthesis) form a discrete set. In these the effects of alkyl groups are minimal and their spectra are not greatly different from that of nitrobenzene (curve 6). In contrast the absorption curves for the ortho series (curves 7–10) show widely divergent forms. The most significant feature is the progressive decrease in intensity of the principal absorption band in the order, according to ortho substituents, methyl, *i*-propyl, dimethyl, *t*-butyl.

While the variations in intensity in this series, which must be due primarily to steric hindrance, are rather striking the estimation of intensities, which might yield a quantitative measure of the hindrance, is greatly complicated by the overlapping of absorption bands. The overlapping uncertainty is due principally to bands having maxima beyond the short wave length limit of the measurements and which behave in an irregular way as is shown by the crossing of curves. There are also overlapping bands of low intensity at longer wave lengths, ~2900 Å., but these are affected by ortho substituents in the same order as the 2500 Å. band. The peak intensities recorded in Table I are the measured total intensities for the wave lengths indicated; an overlapping correction, if applied, would further reduce these values.

The wave length of the residual nitro-group absorption insofar as it can be determined with any accuracy, is substantially constant throughout the series of ortho-substituted compounds, such variations as are found being within the limit of uncertainty due to overlapping of bands. Although the simple theory of sterically inhibited resonance predicts shifts to shorter wave lengths with increasing hindrance, the absence of such shifts here is not without precedent.[1,2,3]

The absorption spectra were determined with the aid of a Beckman quartz spectrophotometer using quartz cells of 1 cm. path length. The sol-

---

[1] Sherwood and Calvin, THIS JOURNAL, **64**, 1350 (1942). These authors reported on the absorption spectra of the nitrotoluenes, taken presumably in alcohol solution. We have repeated the measurements on these compounds in isooctane solution in order to have comparable data throughout with respect to solvent.

[2] Remington, *ibid.*, **67**, 1838 (1945).

[3] Additional examples of suppressed absorption, not accompanied by wave length shifts, can be found in the work of Rodebush and co-workers [THIS JOURNAL, **62**, 2906 (1940); *ibid.*, **63**, 3018 (1941)] on the spectra of hindered biphenyls. The theoretical aspects of the problem are discussed by Wheland ["The Theory of Resonance," John Wiley & Sons Inc., New York, N. Y., 1944, pp. 161–162.]

vent was isoöctane. It was purified first by treatment with silica gel, as recommended by Graff, O'Connor and Skau,[4] followed by treatment with permanganate according to the procedure given by Remington,[3] and finally by scrubbing with cold sulfuric acid and then washing with water. It was dried over potassium hydroxide and distilled. Solutions of the nitro compounds, having a nominal concentration of 10^{-4} mole per liter, were prepared by the method of successive dilutions by weight. For each compound at least two independent sets of observations were made.

Except for minor deviations in procedure, the compounds, if not commercially available, were prepared by methods described in the literature. Purification was effected by fractional distillation under vacuum or by fractional crystallization or by a combination of both as in each case was appropriate. The purification was deemed adequate when further processing resulted in no further measurable changes in the absorption spectra. Since these materials darken on standing, the spectra were determined on freshly purified specimens. The physical constants are given in Table I.

TABLE I

PHYSICAL CONSTANTS AND ABSORPTION MAXIMA

Compound	M. p., °C.	$n^{20}D$	$\lambda_{max.}$, Å.	$\epsilon_{max.}$
Nitrobenzene	5.5	1.5528	2520	8620
o-Nitrotoluene	−10.5	1.5471	2500	5950
m-Nitrotoluene	15.5	1.5468	2565	8160
p-Nitrotoluene	52	....	2640	10250
o-Nitrocumene	103[a]	1.5259	2470	3760
p-Nitrocumene	122[a]	1.5367	2650	10430
o-Nitro-*t*-butylbenzene	−3	1.5171	No maximum[b]	
m-Nitro-*t*-butylbenzene	2	1.5268	2580	8220
p-Nitro-*t*-butylbenzene	28.2	1.5338	2650	10720
Nitromesitylene	43.4	....	No maximum[c]	

[a] B. p. at 9 mm. [b] At 2500 Å. ϵ is 1450. [c] At 2500 Å. ϵ is 2060.

The extraordinary sensitivity of *o*-nitrocumene to photochemical oxidation is not commented upon by Sterling and Bogert[5] who first isolated the pure compound. When the compound, or a solution of it in a hydrocarbon solvent, is exposed a deep red color develops and from a solution in low boiling petroleum ether the product separates in the form of brilliant red crystals, the identity of which is not yet known. The substance is markedly less sensitive to light when in alcohol solution, and it appears to be indefinitely stable in the dark.

The attempted synthesis of *m*-nitrocumene by the conventional scheme for *m*-nitroalkylbenzenes failed because of difficulties in the nitration of *p*-acetylaminocumene. On attempting nitration of a crude acetylation product in glacial acetic acid following a procedure similar to that of Fanta and Tarbell[6] the mixture being heated to 60° for a short time and then allowed to stand overnight, the only recoverable product was unchanged *p*-acetylaminocumene. On treatment with a nitrating mixture of sulfuric and nitric acids at 35° a moderately vigorous reaction occurred with the evolution of nitrogen oxides and the product was identified as *p*-nitroacetanilide. The same product was obtained in excellent yield when the temperature was maintained at 0–5° during the reaction. The elimination of *i*-propyl groups on nitration has been recorded previously in several instances.[7,8]

Summary

The ultraviolet absorption spectra of the mononitro derivatives of toluene, cumene, *t*-butylbenzene and mesitylene are reported. Anomalous intensities, observed in the ortho-substituted series, are correlated with the effectiveness of the various alkyl groups in suppressing nitro-group resonance.

CHICAGO, ILLINOIS RECEIVED JANUARY 2, 1947

---

(4) Graff, O'Connor and Skau, *Ind. Eng. Chem., Anal. Ed.*, **16**, 556 (1944).

(5) Sterling and Bogert, *J. Org. Chem.*, **4**, 20 (1939).

(6) Fanta and Tarbell, "Organic Syntheses," **25**, 78 (1945).

(7) Newton, THIS JOURNAL, **65**, 2434 (1943).

(8) Doumani and Kobe, *J. Org. Chem.*, **7**, 1 (1942).