[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOYOLA UNIVERSITY OF CHICAGO]

EFFECTS OF STERIC HINDRANCE ON ULTRAVIOLET ABSORP-TION SPECTRA AND IONIZATION CONSTANTS THROUGH MONO-AND DI-ALKYL SUBSTITUTION IN 2,4,6-TRINITROPHENOL

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In the course of the study of the reagent properties of some *meta*-substituted 2,4,6-trinitrophenols it was suggested that we obtain information on the pK_a values and ultraviolet absorption spectra because some of the compounds under study are not easily accessible and these data, which are of interest in structural organic chemistry, are not in the literature. These data are herewith presented.

DISCUSSION

Since the nitro groups in 2,4,6-trinitrophenols lie in the plane of the benzene ring, *meta*-substituents offer strong hindrance to the nitro groups adjacent to them and thus affect the position of the absorption maxima, the intensity of the absorption, and the size of the ionization constants.

The pK_a values, except for pictic acid which was already in the literature, were determined by potentiometric titration and are summarized in Table I.

An examination of Table I shows that picric acid is about as strong an acid as the mineral acids but that the introduction of a methyl group to form methylpicric acid lowers its acidity by about one hundred fold. The substitution of the larger ethyl group for the methyl has little additional effect. This fact may indicate that the terminal carbon of the ethyl group is out of position to offer any great amount of additional hindrance. A photograph of a Fischer-Herschfelder model of ethylpicric acid in Figure 1 shows the most probable position of the ethyl group as being one with the terminal CH₃ out of the plane of the ring.

The introduction of two methyl groups to form dimethylpicric acid results in a significant decrease in acidity over the two cases just cited. The combination of methyl-ethyl groups in ethylmethylpicric acid gives an acid about as strong as the dimethylpicric acid since the terminal carbon atom of the ethyl group probably is not in position to offer much additional hindrance.

The isopropyl group appears to offer very strong hindrance, as would be expected, and yields an acid of the same order of acidity as the compounds with di-substituents.

In the spectra of picric acid in isoöctane three absorption bands appear be-

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TABLE I											
pK.	VALUES	OF	Some	2,4,6-TRINITROPHENOLS							

Compound	$p K_{a}$
Pierie aeid.	0.96
Methylpicric acid	2.8
Ethylpieric acid	3.0
Dimethylpicric acid	3.3
Methylethylpicric acid	3.3
Isopropylpicric acid	3.4



FIG. 1. PHOTOGRAPH OF FISCHER-HERSCHFELDER MODEL OF ETHYLPICRIC ACID

tween 220 and 400 m μ (Fig. 2). The most intense band of picric acid, which occurs at the shortest wave length, does not appear in the spectra of the alkyl-substituted picric acids in the region 220–400 m μ . It is possible that this band has undergone hypsochromic displacement into the vacuum ultraviolet.

The decreased intensity observed for all mono- and di-alkyl substituted compounds is probably from the steric interaction with an adjacent resonating group. This type of steric interaction is well known (1–3). This substitution should reduce the possibility of achieving those contributing structures which are contingent on resonance of the π -orbital electrons of atoms in a planar configuration. The molar extinction coefficients at the absorption maxima of the compounds under study are summarized in Table II.

The small bathochromic displacement of the most intense absorption bands of the alkyl-substituted trinitrophenols which occurs at the shorter wave length is that expected of an electron contributing group. Such a shift implies a decrease



FIG. 2. PLOT OF WAVE LENGTH versus LOG MOLAR EXTINCTION COEFFICIENT. Picric Acid -----; Methylpicric Acid -----.

TABLE II

Molar Extinction Coefficients of Some 2,4,6-Trinitrophenols at the Absorption Maxima

Compound	Log e	λ _{max}	Log e	λ _{max}	Log e	λ_{max}
	max	(mμ)	max	(mμ)	max	(m μ)
Picric acid Methylpicric acid Ethylpicric acid Isopropylpicric acid Dimethylpicric acid Ethylmethylpicric acid	4.23	230	$\begin{array}{r} 4.18 \\ 4.00 \\ 4.10 \\ 4.01 \\ 3.76 \\ 3.88 \end{array}$	254 257 257 266 272 274	$\begin{array}{r} 3.62 \\ 3.54 \\ 3.53 \\ 3.59 \\ 3.20 \\ 3.60 \end{array}$	340 335 335 340 350 345

in the energy level differences between ground and excited states. This difference is the result either of the lowering of the energy of the excited state, the raising of the energy of the ground state, or a combination of both.

This uniform effect is not found for the absorption bands at the longer wave lengths. The mono-substitutions all result in slight hypsochromic effects, whereas



FIG. 3. PLOT OF WAVE LENGTH versus LOG MOLAR EXTINCTION COEFFICIENT. Picric Acid -----; Ethylpicric Acid -----.



FIG. 4. PLOT OF WAVE LENGTH versus LOG MOLAR EXTINCTION COEFFICIENT. Picric Acid -----; Isopropylpicric Acid -----.



FIG. 5. PLOT OF WAVE LENGTH versus LOG MOLAR EXTINCTION COEFFICIENT. Picric Acid -----; Dimethylpicric acid ——.



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the di-substitutions produce bathochromic displacements. Steric interference with resonance usually causes increased shifts to shorter wave lengths with increasing hindrance. However, the absence of such shifts and displacements in the opposite direction are well known (3-6).

The curves of λ vs log molar extinction coefficient are shown in Figures 2-6.

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EXPERIMENTAL

Preparation of compounds. Picric acid. Bakers Analyzed picric acid was recrystallized several times from hot benzene and was dried for four hours at 78° under a high vacuum in an Abderhalden drying pistol; m.p. 122° (uncorrected).

Methylpicric acid. m-Cresol (10 g.) dissolved in 100 ml. of concentrated sulfuric acid was heated to 60° and cooled in an ice-salt bath to 10°. The solution was rapidly agitated and 50 ml. of concentrated HNO₃ was added at such a rate that the temperature did not exceed 20°. The reaction product was poured over 50 g. of crushed ice and the crude phenol was collected. Then 5 g. of the crude product was dissolved and recrystallized several times from 15-ml. portions of alcohol. The purified product was dried under a high vacuum in an Abderhalden drying pistol (7), m.p. 106° (uncorrected).

Ethylpicric acid. This acid was prepared from 3-ethylphenol as described above and was recrystallized from hot ethyl alcohol and dried in an Abderhalden drying pistol and the purity was checked by analysis; m.p. 87.5° (uncorrected).

Dimethylpicric acid. This compound was prepared by nitrating m-xylenol in the manner described above, was recrystallized from hot water, and was dried in an Abderhalden drying pistol (8), m.p. 106.5° (uncorrected).

Ethylmethylpicric acid. This compound was prepared by the nitration of 1,3,5-ethylmethylphenol as described in the above procedure. Then 5 g. of the crude nitrophenol was dissolved in 15 ml. of ether. Petroleum ether (25 ml.) was added and the solution was warmed cautiously on the steam-bath to remove most of the ethyl ether. The remaining solution was cooled in an ice-salt bath and the crystals were removed. After several recrystallizations the crystalline product was dried under high vacuum in an Abderhalden drying pistol (9), m.p. 67.0° (uncorrected).

Isopropylpicric acid. The trinitrophenol was prepared as described above and was recrystallized four times from hot alcohol; m.p. 122.5° (uncorrected).

Anal. Calc'd for C₉H₉N₃O₇: C, 39.86; H, 3.35; N, 15.50.

Found: C, 40.27; H, 3.02; N, 15.16.

Determination of ionization constants. The ionization constants were determined by potentiometric titration of dilute aqueous solutions of the free nitrophenols with 0.05 N NaOH. The titration data were obtained by use of a Beckman Model G pH meter equipped with a general purpose glass electrode and the saturated calomel electrode. Clark and Lubs buffers were used throughout for standardization purposes. Since the solutions titrated were dilute, the pK_s values were not corrected for ionic strength effects.

Determination of ultraviolet spectra. The spectra were determined with a Beckman spectrophotometer, Model DU, which was equipped with a photomultiplier tube, (1P28) in place of the usual blue sensitive tube, 1-cm. silica cells, and a hydrogen lamp as a light source.

The solvent used in all these experiments was spectral purity grade isoöctane (2,2,4-trimethylpentane) which was supplied by the Phillips Petroleum Company.

Molar extinction coefficients were calculated from the equation:

$$\epsilon = \frac{AM}{bc}$$

where: A is the absorbance, b the cell thickness in centimeters, M the molecular weight, and c the concentration in grams per liter.

SUMMARY

Ultraviolet absorption spectra and ionization constants were determined for picric acid and five alkyl-substituted 2,4,6-trinitrophenols.

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