After washing with water and drying over Drierite, the crude product was distilled to yield 168 g. (77%) of C_3F_7-$CFCl_2$, b.p. 62.8°.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

The Structure of Kornatzki's Nitrotoluenedisulfonic Acid

BY JOHN W. MORTON AND J. E. CALLEN

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In 1883, Kornatzki[1] reported the sulfonation of *p*-bromotoluene to yield a disulfonic acid which, on treatment with concentrated nitric acid, was converted into a nitrotoluenedisulfonic acid. The 4-nitro-2,6-disulfo structure (I) has been assigned, without proof, to the latter compound.[2] It appeared desirable to investigate the structure of Kornatzki's nitro compound. Even on the assumption that the bromotoluenedisulfonic acid intermediate was the 4-bromo-2,6-disulfo compound,[3] the possibility of rearrangement during the reaction with nitric acid cannot be excluded.[4] We have carried out reactions with Kornatzki's nitro compound which confirm the structure I. The nitrotoluenedisulfonic acid, which was isolated as the potassium salt, first was converted into the disulfonyl chloride. A highly purified sample of the chloride was hydrolyzed, and the acidic product reconverted to the potassium salt, whose infrared absorption spectrum proved to be identical with that of the original potassium salt, establishing the isomeric purity of the product. Reduction of the disulfonyl chloride to the disulfinate, and conversion of this into the bischloromercuri compound and finally into the known[5] 4-nitro-2,6-dibromotoluene, completed the confirmation of structure.

Through a similar sequence of reactions, the disulfonyl chloride was used to prepare the hitherto unreported 4-nitro-2,6-diiodotoluene.

Acknowledgments.—The authors are grateful to Dr. Alexander Ritchie of Thomas Hedley & Co., Ltd., Newcastle-on-Tyne, England, for experimental details concerning the preparation and purification of the Kornatzki product. They are indebted also to a number of members of this Laboratory for experimental assistance.

Experimental[6]

Potassium 4-Nitrotoluene-2,6-disulfonate.[1]—A mixture of 156 g. (82 ml.) of 20% oleum and 468 g. (246 ml.) of sulfur trioxide (totaling 499 g., or 6.2 moles, of sulfur trioxide) was added with stirring over a period of one to 1.5 hours to 260 g. (1.52 moles) of *p*-bromotoluene and the temperature of the mixture rose to about 130°. The sulfonation mixture (which usually solidified on cooling) was quenched in ice-water and neutralized with lime. The calcium sulfate was filtered off, and the cake was thrice washed with boiling water. The combined filtrate and washings were evaporated to 2.5 l., diluted with 1.5 l. of methanol, and 50% sulfuric acid was added to the resulting mixture until precipitation ceased. Precipitated calcium sulfate was filtered off and washed as before, and the combined filtrate and washings were concentrated to a volume of two liters and made neutral to litmus by the addition of barium carbonate. After filtration and copious washing, the resulting solution of barium bromotoluenedisulfonate was concentrated to 2.5 l., cooled to 10°, and the precipitated barium salt was collected, washed with ethanol and dried. For conversion into the free acid, the barium salt was slurried in water and treated with dilute sulfuric acid until no further precipitation occurred. The precipitate was filtered off and washed, and filtrate and washings were evaporated to dryness on the steam-bath to yield 190–220 g. (38–44%) of free acid, as a tenacious mat of almost-white material melting diffusely over the range 140–150°.

This material was refluxed for 16 hours with 2.8 times its weight of 95% nitric acid, and the reaction mixture was evaporated on the steam-bath to remove excess nitric acid. The residue, which sometimes solidified on cooling, was dissolved in 1.5 l. of water and neutralized with barium carbonate. Solid material was filtered off and washed with much boiling water, and the combined filtrate and washings were evaporated to 1 l. and cooled to 10° to obtain a precipitate which was collected and washed with ethanol. The combined filtrate and washings were treated with potassium carbonate until precipitation had ceased, and the resulting barium carbonate was filtered off and washed with boiling water. Evaporation to dryness of the combined filtrate and washings left a brown residue which was extracted eight times with boiling 95% ethanol and then recrystallized from water to yield 6–17 g. (1.1–3.0%, based on *p*-bromotoluene) of potassium 4-nitrotoluene-2,6-disulfonate ranging from tan to white in color.

Anal. Calcd. for $C_7H_5K_2NO_8S_2$: C, 22.52; H, 1.35; K, 20.95; N, 3.75; S, 17.16. Found: C, 22.47, 22.71; H, 1.27, 1.35; K, 20.86, 20.90; N, 3.85, 3.72; S, 17.17, 17.24.

4-Nitrotoluene-2,6-disulfonyl Chloride.—The free disulfonic acid, obtained by exchanging a 1% solution of the potassium salt on a column of Amberlite-120 resin, was heated on the steam-bath overnight with 3.5 times its weight of phosphorus pentachloride. The resulting solution was poured over ice, and the solidified product was filtered off and air-dried. Recrystallization from isoöctane gave an average yield of 67% of product, m.p. 112.5–113.5°. Repeated recrystallizations led to a constant m.p. of 114.5–115.0°.

Anal. Calcd. for $C_7H_5Cl_2NO_6S_2$: C, 25.18; H, 1.51; Cl, 21.23; N, 4.18; S, 19.19. Found: C, 25.23; H, 1.44; Cl, 21.03; N, 4.21; S, 19.15.

A highly purified sample of the dichloride was hydrolyzed by heating with water in a sealed tube for 5.5 hours at 150°. Evaporation of the resulting homogeneous solution left a white residue which was neutralized with aqueous potassium hydroxide. Addition of ethanol precipitated the potassium salt, whose infrared absorption spectrum showed it to be identical with the potassium salt from which the sulfonyl chloride had been prepared.

Conversion of the Disulfonyl Chloride to 4-Nitro-2,6-dibromotoluene.—To 5.0 g. (0.015 mole) of the disulfonyl chloride in a nitrogen-swept vessel was added a solution of 4.0 g. (0.0318 mole) of sodium sulfite in 30 ml. of water, with stirring. As the highly exothermic reduction proceeded, sodium hydroxide was added as necessary to maintain alkalinity. The reaction continued for about 30 minutes, during the last 20 of which the mixture was heated in a water-bath. Then a little hydrochloric acid was added to make the disulfinate solution barely acidic, and the mixture was poured into a hot solution of 17.2 g. (0.0636 mole) of mercuric chloride in about 30 ml. of water. The resulting clear orange solution deposited a copious precipitate after about ten seconds, and the odor of sulfur dioxide was noticed. After heating for 30 minutes, the mixture was filtered hot, and the residue washed with hot water and dried to yield 5.8 g. (64%) of crude mercury compound. This product,

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[1] O. Kornatzki, *Ann.*, **221**, 191 (1883).

[2] Beilstein's "Handbuch," Vol. 11, p. 207.

[3] The likelihood of more than one orientation in reactions of this type is emphasized by the fact that oleum sulfonation of *p*-bromotoluene has been shown to yield a mixture of 2- and 3-sulfonic acids, and that potassium 4-chlorotoluene-2-sulfonate on oleum treatment yields a mixture of the 2,5- and the 2,6-disulfo compounds. See C. M. Suter in R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 168–169.

[4] The formation of a dibromonitrotoluenesulfonic acid as one of Kornatzki's by-products[1] illustrates the ability of groups to wander under the conditions of the reaction with nitric acid.

[5] R. H. C. Nevile and A. Winther, *Ber.*, **13**, 973 (1880); **14**, 419 (1881).

[6] All melting points are uncorrected. Analyses by Huffman Microanalytical Laboratories.

without further purification, was converted into the dibromo compound by shaking for 20 hours with a solution of 2.74 g. of bromine in 20 ml. of carbon tetrachloride. The reaction mixture was washed with aqueous sulfite and then with water, and finally filtered and evaporated to dryness. The residue was taken up in petroleum ether (b.p. 35–60°) and chromatographed on a 40-g. alumina column, using more solvent as eluent. A single solid fraction consisting of 0.706 g. (18.6%, based on sulfonyl chloride), m.p. 55.0–56.5°, was isolated. Recrystallization from methanol yielded 0.409 g. (11%) of light yellow crystals, m.p. 57.0–57.5°. A mixed melting point with an authentic specimen of 4-nitro-2,6-dibromotoluene was not depressed, and the infrared absorption spectra of the two samples were identical.

4-Nitro-2,6-diiodotoluene.—Five grams (0.015 mole) of 4-nitrotoluene-2,6-disulfonyl chloride was converted to the bischloromercuri compound as described in the preceding section. The mercury compound was stirred overnight with a suspension of 4.2 g. of iodine in carbon tetrachloride. Excess iodine was destroyed by washing the mixture with aqueous sodium sulfite. The organic layer was filtered and evaporated to dryness, and the residue was taken up in a 1:4 mixture of benzene and petroleum ether (b.p. 35–60°) and chromatographed on alumina, using benzene–petroleum ether mixtures of increasing benzene content for elution. The only sizable fraction recovered was 0.293 g. (5.0%) of light yellow crystals, m.p. 116°.

Anal. Calcd. for $C_7H_5I_2NO_2$: C, 21.61; H, 1.30; I, 62.26. Found: C, 21.61; H, 1.34; I, 65.35.

PROCTER AND GAMBLE CO.
MIAMI VALLEY LABORATORIES
CINCINNATI 31, OHIO

Quantum Mechanical Calculations of Electrical Effects of Substituents in *para*-Substituted Anilines

BY JOHN D. ROBERTS AND DOROTHY A. SEMENOW

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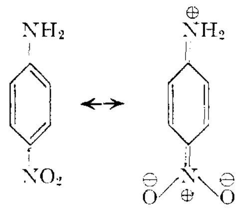
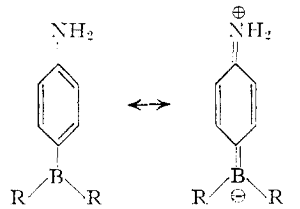
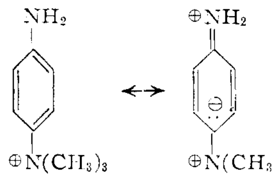
Base strength measurements with substituted anilines indicate direct conjugation between the amino groups and electron-attracting unsaturated substituent groups such as $-NO_2$, $-C{\equiv}N$, etc. (I). Such conjugation delocalizes the unshared electron pair of nitrogen and confers a formal (+) charge on the amino group. Somewhat analogous behavior might be anticipated for substituents which do not carry multiple bonds but which, like tercovalent boron, could accept an electron pair (II) or, like a positively charged trimethylammonium group, could stabilize an adjacent negatively charged center as in the "ylides" (III). Resonance forms may be written which symbolize each of these situations (I–III).



I



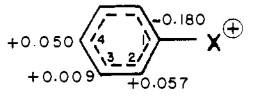
II



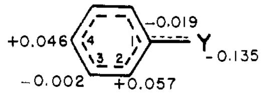
III

In order to determine whether the extent of delocalization of the unshared pair of electrons on nitrogen in *para*-substituted anilines is, at least theoretically, dependent on the character of the substituent, calculations were made by the simple molecular orbital method[1] of the charges on the amino nitrogen in such compounds where the *para*-substituent is: (1) $-X^{\oplus}$ bearing a unit positive charge (analogous to $-N(CH_3)_3^{\oplus}$); (2) $-Y$ carrying an empty p-orbital (analogous to $-BR_2$); and (3) $-\overset{|}{C}{=}Z$ where Z (analogous to oxygen) is more electronegative than carbon and the polarization of the $-\overset{|}{C}{=}Z$ p-π-bond results in an incompletely filled p-orbital on carbon. The substituent $-X^{\oplus}$ is regarded as being formally unable to "conjugate" with a *para*-amino group, whereas $-Y$ and $-\overset{|}{C}{=}Z$ are both able to take part in such conjugation. $-Y$ and $-\overset{|}{C}{=}Z$ differ from each other only in the degree of unsaturation of the p-orbitals (on Y and C, respectively) and in the electron affinities of Y and Z.

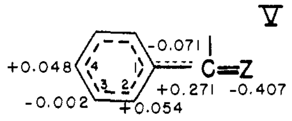
The condition was imposed that systems IV, V and VI have nearly the same charge (*e.g.*, +0.05 of an electron charge[2]) in the π-electrons at C_4 before introduction of a *para*-amino group, so that the only important variable in the *para*-substituted anilines is the electron-accepting power of the substituent.



IV



V



VI

This was achieved by assigning appropriate coulomb integrals, $\alpha + \delta\beta$, to atoms having electron affinities different from a "normal" carbon atom with coulomb integral α; $\delta > 0$ for larger and $\delta < 0$ for smaller electron affinities than a "normal" carbon atom. The δ values used for atoms adjacent to the source of polarization[3] (*i.e.*, C_2 and C_6 in IV, C_1 in V and C_7 in VI) were one-tenth the δ values for the atom at the source (*i.e.*, C_1 in IV, Y in V and Z in VI); coulomb integrals for which δ was less than 0.05 were set equal to α. Resonance integrals between non-adjacent atoms were neglected and, in general, those between adjacent atoms were assigned a value of β. Coulson[4] has stated that the deviation from β of resonance integrals involving

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(1) (a) E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättiger und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 77–85; (b) C. A. Couson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); (c) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. X11I.

(2) The charge at C_4 was chosen to be equal to 0.05 of an electron charge since then a substance possessing the over-all charge distribution of VI would have a resonance moment of 0.4 *D* which is of the same order of magnitude as the experimental resonance moments, 0.3 and 0.6 *D*, for benzaldehyde and benzonitrile, respectively.

(3) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

(4) C. A. Coulson, "Valence," Oxford University Press, London 1952, p. 242.