paper showed no presence of peroxides. The mixture was diluted with a large volume of water. The ether layer was separated and washed once with water. The ether was evaporated and the residue was dissolved in an equal volume of petroleum ether. Fifty cc. of saturated sodium bisulfite solution was added and the mixture was shaken on a shaking machine for two hours. The bisulfite addition product was washed well with petroleum ether, transferred to a separatory funnel and well shaken with 200 cc. of 10% sodium carbonate solution until all the solid material dissolved. The mixture was extracted with petroleum ether. The petroleum ether layer was dried and the solution was fractionated, collecting the material from 168–171°; yield 9 g.; d^{20} 0.8149; $n^{20}D$ 1.4150. *Anal.* Calcd.: C, 74.98; H, 12.59. Found: C, 74.60; H, 12.54.

Methyl Isohexyl Ketone Semicarbazone.—One gram of the ketone was dissolved in 5 cc. of alcohol and floated on 5 cc. of a solution containing 1 g. of semicarbazide hydrochloride and 1 g. of sodium acetate. The tube was heated to 60° and the contents rapidly mixed. On cooling, a heavy crystalline precipitate of the semicarbazone was obtained and filtered off. The product was recrystallized from dilute alcohol; m. p. 146–147°. *Anal.* Calcd.: C, 58.35; H, 10.34. Found: C, 58.38; H, 10.00.

3,7-Dimethyloctene-2 Oxide.—0.33 mole of benzoyl hydrogen peroxide in 635 cc. of chloroform was added slowly to 40 g. of the hydrocarbon at 0°, and the mixture was allowed to stand overnight at 0°. Titration showed that 0.30 mole of the benzoyl hydrogen peroxide had been used (one double bond). The solution was washed with dilute sodium carbonate, dried over anhydrous potassium carbonate. The chloroform was recovered and the residue was distilled; yield 40 g. of a product boiling from 179–183°; d^{23} 0.8183; $n^{26}D$ 1.4290.

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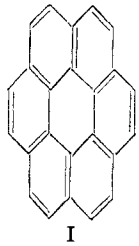
BROOKLYN, N. Y. RECEIVED MARCH 3, 1942

The Ultraviolet Absorption Spectra of Coronene

BY JOHN W. PATTERSON

Coronene, I, is the simplest hydrocarbon in which benzene rings completely surround a central aromatic nucleus. It is the most symmetrical of the more complex aromatic hydrocarbons and as such its absorption spectrum is of particular interest.



I

The sample, which was kindly furnished by Dr. Newman[1] was a synthetic preparation of greater purity than has hitherto been available. In making the ultraviolet absorption measurements, it was necessary to use chloroform as a solvent,

TABLE I

POSITIONS AND INTENSITIES OF BANDS IN CORONENE

Fresnels, f.	Wave number, cm.$^{-1}$	Wave length, mμ	Extinction, $\log_{10} E$ molar
697	23,200	431	2.23
710	23,600	422	2.15
730	24,300	411	2.60
743	24,700	404	2.50
770	25,600	389	2.50
785	26,100	382	2.49
795	26,400	377	2.49
844	28,000	355	3.00
863	28,700	347	4.06
880	29,300	441	4.74
895	29,800	335	4.21
920	30,600	326	4.35
950	31,600	316	4.40
985	32,800	305	5.44
1002	33,400	299	4.98
1025	34,100	293	4.87
1065	35,400	282	4.29

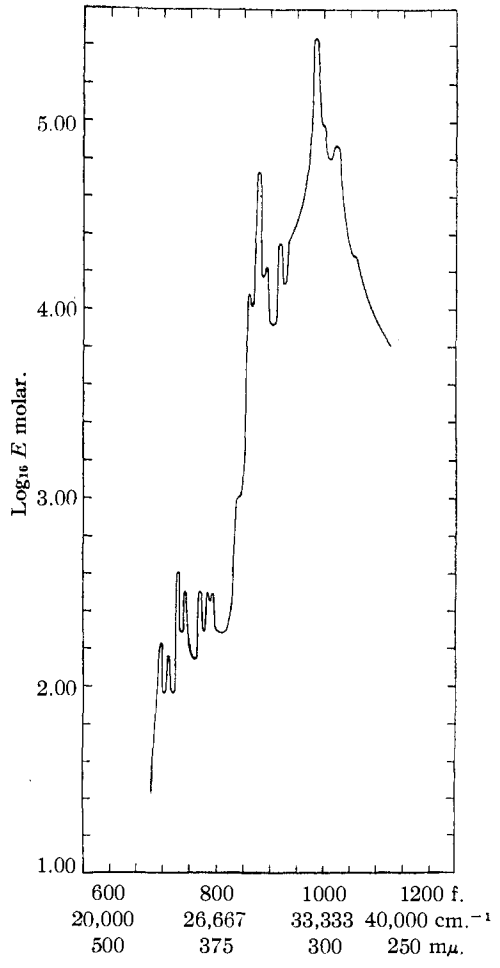


Fig. 1.—Ultraviolet absorption spectra of coronene.

(1) Newman, THIS JOURNAL, **62**, 1683 (1940).

but aside from this the technique used was the same as has been reported previously.[2] The results obtained are recorded in Table I and Fig. 1. They indicate the usefulness of the absorption spectrum as a means of identification of coronene.

(2) Brode and Patterson, THIS JOURNAL, **63**, 3252 (1941).

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RECEIVED APRIL 30, 1942

The Preparation of Acetylsalicylyl Disulfide and Salicylyl Disulfide

BY BYRON RIEGEL AND HAROLD WITTCOFF[1]

Benzoyl disulfide has been reported to be efficacious[2] in the treatment of pruritus. In order to combine the seemingly advantageous features of the aspirin and salicylic acid residues with the disulfide linkage, the *o*-hydroxy and *o*-acetoxybenzoyl disulfides were prepared.

The most direct method of synthesis is the oxidation of the sodium salt of the thio acid, which is prepared by the interaction of the acid chloride and anhydrous sodium hydrogen sulfide. A good method for the preparation of aspiryl chloride which gave a 91% yield of material that melted at 60° in contrast to the value of 49–50° given by Lindemann and Schultheis[3] involved merely the action of purified thionyl chloride on acetylsalicylic acid catalyzed by a few drops of dry pyridine. The addition of hydrogen sulfide to an anhydrous ethanolic solution of sodium ethoxide proved to be a convenient method for the preparation of an anhydrous solution of sodium bisulfide (NaSH). When the acid chloride was added to the ethanolic solution of sodium bisulfide, an unexpected loss of the acetyl group occurred simultaneously with the formation of sodium thiosalicylate even though the bisulfide solution was acid to phenolphthalein. The sodium salt was oxidized directly to the desired disulfide by the addition of iodine to the alcoholic solution, from which the crystalline product precipitated immediately. On crystallization from ethylene chloride the salicylyl disulfide melted at 142°. Acetylation of this product gave acetylsalicylyl disulfide which on crystallization from 95% ethanol melted at 101.2°. In some respects this method is similar to that given by Moness, Lott and Christiansen[4] for the preparation of benzoyl disulfide.

Toxicity and skin irritation tests on these two compounds were performed by Dr. Edwin J. Fellows, Department of Pharmacology, Temple University, School of Medicine. He found them to be non-irritant when ointments in 25% concentration, with either petrolatum or hydrophilic base, were applied to the shaved skin of rabbits. Likewise acacia or fixed oil suspensions of these compounds, when injected intramuscularly into rats in doses of 400–800 mg. per kg. of body weight were non-toxic. However, preliminary clinical tests as antipruritics have not proved encouraging.

Experimental[5]

Acetylsalicylyl Chloride.—In a flask equipped with a reflux condenser which was connected to a gas trap was placed 100 g. of acetylsalicylic acid (aspirin), 1 g. of dry pyridine and 78 g. (10% excess) of thionyl chloride, purified by distillation from cottonseed oil. Gentle heating on a steam-bath initiated the reaction. Heating was then discontinued until gas no longer was evolved, after which the reaction mixture was refluxed for one-half hour. On distillation at 5 mm., 100 g. (91%) of colorless liquid was obtained which distilled at 115°. The acetylsalicylyl chloride solidified on long standing. Crystallization from dry benzene gave thick prisms which turned milky at 52° and fused to a clear liquid at 60°. Later it was found that the undistilled reaction product was of sufficient purity for the subsequent reactions.

Salicylyl Disulfide.—An ethanolic sodium hydrosulfide solution[6] was prepared by saturating with hydrogen sulfide a solution of 125 g. of sodium in two liters of anhydrous ethanol. Hydrogen sulfide addition, even though facilitated by mechanical shaking, required several days. The solution assumed a brilliant yellow color and did not redden moistened phenolphthalein paper. This solution, after filtering, was used directly for the next reaction.

The best yields were obtained when one mole of the acid chloride reacted with two moles of the sodium hydrosulfide. Since the acetyl groups were removed it seemed that stoichiometrical proportions of sodium hydrosulfide, four moles, should be used; however, this gave much poorer results. To an ice cold solution containing a two molar equivalent of sodium hydrosulfide was added 110 g. of acetylsalicylyl chloride slowly with stirring. There was an evolution of hydrogen sulfide, and sodium chloride and presumably sodium acetate precipitated. The suspension was centrifuged and the precipitate was washed two times with small quantities of anhydrous ethanol. To the yellow

(1) Smith, Kline and French Research Fellow.

(2) (a) L. Bory and M. Mesanguy, *Bull. soc. franc. dermatol. syphilig.*, **46**, 344 (1939); (b) L. A. Brunsting, *Collected Papers of the Mayo Clinic and the Mayo Foundation*, **32**, 768 (1940); (c) S. Amberg and L. A. Brunsting, *Military Surgeon*, **88**, 617 (1941).

(3) (a) H. Lindemann and W. Schultheis, *Ann.*, **451**, 241 (1927); (b) R. Anschütz, *ibid.*, **367**, 172 (1909); see also the following who did not record a melting point: (c) J. McConnan and A. W. Titherley, *J. Chem. Soc.*, **89**, 1333 (1906); (d) R. Wolffenstein, German Patent 277,659; (e) I. M. Heilbron and D. W. Hill, *J. Chem. Soc.*, 1705 (1927).

(4) E. Moness, W. A. Lott and W. G. Christiansen, *J. Am. Pharm. Assoc.*, **25**, 397 (1936).

(5) All melting points are corrected. Microanalyses are by Dr. T. S. Ma, University of Chicago.

(6) A. Rube, *J. Chem. Soc.*, **99**, 558 (1911).