

benzene in hexane. The first fraction contained 101 mg. of solid, m.p. 53–67°; recrystallization yielded 65 mg. of essentially pure 1,1,1-triphenylethane, m.p. 88–92°. Fraction 2 weighed 148 mg., m.p. 48–50°, and was essentially pure 1,1,2-triphenylethane. Fraction 3 contained 330 mg., m.p. 47–50°; recrystallization from hexane gave 300 mg. of 1,1,2-triphenylethane, m.p. 51–53°. Fraction 4 weighed 95 mg. and melted at 45–48°. Crystallization brought the m.p. to 50–52°, wt. 85 mg. Fraction 5 yielded 44 mg., m.p. 35–42; the infrared spectrum indicated this to be only slightly impure 1,1,2-triphenylethane. The identity and purity of the crystallized products obtained from fractions 1, 3 and 4 were checked by infrared analysis. Thus 617 mg. of the 1,1,2-triphenylethane chromatographic fraction was obtained while only 101 mg. of the 1,1,1-triphenylethane fraction was isolated; the crystallized yields totaled 533 mg. of 1,1,2-triphenylethane and 65 mg. of 1,1,1-triphenylethane.

In a second run the reaction time was reduced to 5 hr.; 1.34 g. of crude product was isolated. Chromatography was effected on silica gel (31 × 730 mm.) slurry packed with 10% ether in hexane and washed with hexane. Seven 200-ml. fractions were collected by elution with hexane followed by an eighth and ninth using 10% ether in hexane. Fraction 4 contained 110 mg. of material seen from the infrared to be impure 1,1,1-triphenylethane. Fraction 5 yielded 412 mg. of similar material. Fraction 6 gave 349 mg. of a mixture of 1,1,1-triphenylethane and 1,1,1-triphenyl-2-chloroethane. Fraction 7 afforded 195 mg. of essentially pure 1,1,1-triphenyl-2-chloroethane and 8 gave 120 mg. of similar material. Crystallization of the material from fractions 4 and 5 brought the m.p. to 92–94°. The final filtrates indicated small amounts of 1,1,2-triphenylethane. Crystallization of the material from fractions 7 and 8 brought the m.p. to 97–99° with a little loss to the filtrate.

In a third run the reaction time was only 2.5 hr. The crude product, isolated as before, was chromatographed on silica gel (1100 × 23 mm.) packed with hexane; 24 50-ml. fractions were collected by elution with 25% benzene in hexane. Fractions 10 through 13 crystallized and were found to be essentially pure 1,1,1-triphenylethane, total wt. 276 mg. Fraction 14 weighed 26 mg. and was found to be a mixture of triphenylethylene, 1,1,1-triphenylethane and 1,1,2-triphenylethane. Fractions 15 and 16 totaled 126 mg. and were found to contain both triphenylethylene and 1,1,2-triphenylethane by infrared analysis. Fractions 17 through 24 were solid and melted at 90–94°, wt. 549 mg.; this was shown to be virtually pure 1,1,1-triphenyl-2-chloroethane by infrared analysis.

In a fourth run made for 5 hr. the reaction mixture was poured onto 150 g. of chopped Dry Ice. The acidic fraction weighed 101 mg. and melted at 128–131°; one crystallization brought the melting point to 131–132°. Thus only 2,2,3-triphenylpropanoic acid was formed.

In the reactions of sodium with 1,1,1-triphenyl-2-chloroethane with sodium it was found that for smooth reaction, stirring at 12,000 r.p.m. was necessary; a non-settling sodium dispersion was obtained readily by use of 10 mg. of detergent.

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## Studies of Some Nitro-substituted Benzhydrylcarbonium Ions

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The behavior of the following nitro compounds in 100% sulfuric acid has been studied: 4-nitrobenzhydrol, bis-(3-nitrobenzhydryl) ether, and 3,3'-dinitrobenzhydrol. The first two gave carbonium ions which were rather unstable and readily polymerized. The last gave no visible carbonium ion but did yield a soluble polymer. The properties were investigated utilizing *i*-factors, ultraviolet and near-visible spectra, titration studies, and chemical studies, all using sulfuric acid. Some discussion of the structure and composition of the polymers is presented.

### Introduction

The ionization of benzhydrols<sup>1–5</sup> in 100% sulfuric acid to give stable carbonium ions has been shown to be promoted by electron releasing groups. Electron withdrawing groups should have an effect of decreasing the thermodynamic stability as well as promoting the tendency for polymerization. Since benzhydrol<sup>1</sup> and 3-methylbenzhydrol<sup>2</sup> readily polymerize in 100% sulfuric acid, it was desired to determine the effect of nitro-substitutions on the formation and stabilization of benzhydrylcarbonium ions. It would be predicted that nitrobenzhydrols and bis-nitrobenzhydryl ethers would give unstable carbonium ions in sulfuric acid.

### Results

***i*-Factors.**—Table I gives the *i*-factors as extrapolated to zero time for the compounds studied. Since 4-nitrobenzhydrol and bis-(3-nitrobenzhydryl) ether polymerized rapidly and went into solu-

tion slowly, the *i*-factors were not determined until solution was essentially complete. These solutions required about five or six hours of mechanical shaking at constant temperature. 3,3'-Dinitrobenzhydrol dissolved to give a very pale yellow solution and constant *i*-factors could be determined 40 minutes after addition of the compound to sulfuric acid.

TABLE I

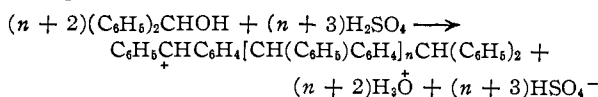
CHARACTERISTICS OF NITRO COMPOUNDS IN SULFURIC ACID

Compound	Color in H <sub>2</sub> SO <sub>4</sub>	Min. % acid <sup>a</sup> for color	Initial <i>i</i> -factors (ex-trapd.)	M.p., °C. of polymer <sup>d</sup>
4-Nitrobenzhydrol	Red-brown	84.3	2.9–3.0 <sup>b</sup>	136–250 <sup>e</sup>
Bis-(3-nitrobenzhydryl) ether	Red-brown	82.8	3.9–4.1 <sup>b</sup>	130–250 <sup>e</sup>
3,3'-Dinitrobenzhydrol	Very faint yellow	89.8	3.03 <sup>c</sup>	170–210 <sup>f</sup>

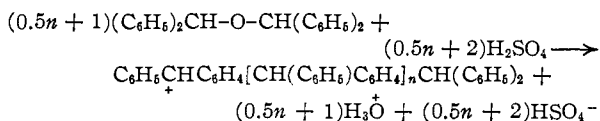
<sup>a</sup> Titration to form visible color with sulfuric acid. <sup>b</sup> Obtained by extrapolation of the straight line portion which began after complete solution was achieved. <sup>c</sup> Value of 3.03 was obtained after 40 minutes and did not change for 17 hours. <sup>d</sup> Melting points were taken on an aluminum melting point block. <sup>e</sup> Darkening occurred at the lower temperature; at the final temperature the polymer had turned black. <sup>f</sup> Darkened at 170° and melted at 210°.

- (1) C. M. Welch and H. A. Smith, *THIS JOURNAL*, **72**, 4748 (1950).
- (2) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3644 (1951).
- (3) H. A. Smith and B. B. Stewart, *ibid.*, **79**, 3693 (1957).
- (4) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).
- (5) H. A. Smith and R. G. Thompson, *THIS JOURNAL*, **77**, 1778 (1955).

The polymerization reaction for benzhydrol can be represented as



The *i*-factor would be  $(2n + 6)/(n + 2)$  for dissolved polymer if no sulfonation occurred. For dimerization,  $n = 0$ , and  $i = 3.0$ . The *i*-factor for a bis ether would be 4.0 for dimerization as shown by



The *i*-factor would be  $(1.0n + 4)/(0.5n + 1)$  for dissolved polymer if no sulfonation occurred. For dimerization,  $n = 0$ , and  $i = 4.0$ . 4-Nitrobenzhydrol and 3,3'-dinitrobenzhydrol gave extrapolated *i*-factors of 3.0 and bis-(3-nitrobenzhydryl) ether gave an extrapolated *i*-factor of 4.0.

**Chemical Studies. Attempted Preparation of Methyl Ethers.**—The sulfuric acid solutions of the compounds when poured into absolute methanol and then into ice-water usually gave only polymeric materials which resembled those obtained from 3-methylbenzhydrol.<sup>8</sup> Different reaction times and concentrations did not yield any methyl ethers. Also the use of an inert solvent for the compounds as described previously<sup>1,3</sup> failed to give any compound but the polymers. Evidently the dimer is formed rapidly and no monomeric carbonium ion is present which can yield the methyl ether. However, in the case of 3,3'-dinitrobenzhydrol in sulfuric acid the original compound, identified by a mixed melting point with the carbinol, was obtained in 60% yield when a reaction time of one minute was used. Longer reaction times gave polymeric materials which were only slightly soluble in the organic phase during the extraction procedure with ethyl ether. It appears that the extractions removed most of the reformed carbinol leaving behind the polymer when a short reaction time was used.

**Reactions of Carbonium Ions with Water.**—The sulfuric acid solutions of the compounds were poured into ice-water mixtures, and the resulting suspensions of polymer were extracted with ether. For a reaction time of one minute, 3,3'-dinitrobenzhydrol gave a 54% yield of the original compound as determined by a mixed melting point. Longer reaction times for this and the other compounds gave only polymeric materials which closely resembled those obtained when the sulfuric acid solutions were poured into absolute methanol first and then into water. Using an inert solvent, different concentrations and different reaction times failed to give any bis ethers, which are the expected products if monomeric carbonium ions were present.

**Titration to Form Carbonium Ions.**—Titrations of the compounds dissolved in an inert solvent and water mixture using 96% sulfuric acid were made to obtain the relative stabilities from the minimum percentage of sulfuric acid necessary for the permanent appearance of the characteristic carbon-

ium ion color. The procedure has been described previously.<sup>5</sup> Titration results are shown in Table I.

### Experimental

***i*-Factors.**—The apparatus, technique and solvent for the cryoscopic measurements have been described previously.<sup>1,9</sup> The runs were made after the compounds had polymerized and dissolved. Solution was effected for 4-nitrobenzhydrol and bis-(3-nitrobenzhydryl) ether by shaking at a fairly constant temperature as described previously.<sup>3</sup>

**Attempted Preparation of Methyl Ethers.**—A 0.25-g. sample of carbinol or bis ether was dissolved in approximately 18 g. of 100% sulfuric acid, and the solution was added immediately to 100 ml. of absolute methanol. The suspension was then poured into 125 g. of an ice-water mixture and extracted quickly with two 100-ml. portions of ether. After drying the ether extracts over Drierite, evaporation of the ether gave the polymeric materials. A large quantity of the polymer remained suspended and was not extracted.

**Reactions of Carbonium Ions with Water.**—A 0.25-g. sample of compound was dissolved in 100% sulfuric acid. The solution was then poured into an ice-water mixture and extracted with several portions of ether. After drying the ether extracts with solid sodium hydroxide pellets, evaporation of the ether gave the polymeric products. A large quantity of the polymer was not extracted. The polymers also were treated with methanol, ethanol or ligroin in the attempt to separate any bis ether which might have been formed. No bis ether was indicated in the products.

The brick-red polymer obtained by adding a sulfuric acid solution of 4-nitrobenzhydrol to an ice-water mixture was collected by filtration. An acetone solution was prepared and dried over anhydrous potassium carbonate for two hours. Evaporation gave a rouge to brick-red compound which was soluble in acetone, tetrahydropyran and nitroethane, but rather insoluble in ethyl ether, ligroin and benzene. The polymer darkened to brown at 136° and black at 145–250°. The molecular weight was determined by the Menzies<sup>7</sup> method. Due to further polymerization in boiling solvents the apparent molecular weight slowly increased after the first equilibrium reading was made. The molecular weight of the compound before extensive polymerization had occurred was 495 which indicates an average chain length of 2.34 benzhydrol units if no reaction with the solvent occurred. However, an elemental analysis indicated that approximately one sulfur was present for each dimer unit. Allowance for this indicates that the main polymer present was the dimer. Since sulfonation would give larger *i*-factors than actually obtained, it appears that solvation of the carbonium ion must have occurred to render the polymers soluble in the sulfuric acid.

**Titration to Form Carbonium Ions.**—The compound was dissolved in 10 ml. of carbon tetrachloride and this solution added to 50 ml. of water. This mixture was then titrated to the barely visible carbonium ion end-point with 96% sulfuric acid. From the volume of acid required, the percentage of acid necessary for visible carbonium ion formation in the aqueous layer was determined. 3,3'-Dinitrobenzhydrol gives only a very faint yellow color even with 100% sulfuric acid.

**Spectra.**—The ultraviolet and near-visible spectra were obtained using a Beckman DU spectrophotometer and quartz cells 1 cm. thick. A hydrogen discharge lamp was used for the range 250–350 mμ; a tungsten filament lamp was used for the range 350–600 mμ. 4-Nitrobenzhydrol and bis-(3-nitrobenzhydryl) ether were dissolved first in cyclohexane to prevent the formation of solid polymer. The method has been used satisfactorily for 3-methylbenzhydrol.<sup>3</sup> The spectra are shown in Fig. 1.

### Preparation of Compounds

**4-Nitrobenzophenone.**—This compound was prepared by the reaction of 4-nitrobenzoyl chloride and benzene in the presence of anhydrous aluminum chloride; carbon disulfide was used as the solvent. A 47.8% yield of pale yellow

(6) L. P. Hammett and A. J. Deyrup, *THIS JOURNAL*, **55**, 1900 (1933); H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

(7) A. W. C. Menzies, *ibid.*, **43**, 2309 (1921); A. W. C. Menzies and S. L. Wright, Jr., *ibid.*, **43**, 2314 (1921).

crystals was obtained. After two recrystallizations from ethanol, the melting point was 139.1–139.2°. A melting point of 138° has been reported.<sup>8</sup>

**4-Nitrobenzhydrol.**—The 4-nitrobenzophenone was reduced by the Meerwein–Pondorf–Verley reaction using commercial aluminum isopropoxide. The synthesis was repeated several times in the attempt to eliminate impurities which might be contributing to the formation of oil. Lund<sup>9</sup> purified this compound by performing several ligroin extractions of the oil. This was also necessary in the present preparation. A yield of 97% of crude material was obtained. The highly purified material melted at 74.5–75.0°. A melting point of 74° has been reported.<sup>9</sup> The higher yields were obtained by using colder and more dilute sulfuric acid to decompose the aluminum complex. The impurities were probably polymers or the bis ether. Other attempted preparations of the benzhydrols have resulted in the formation of bis ethers when sulfuric acid was used to destroy a complex after a lithium aluminum hydride reduction.<sup>5</sup>

**3-Nitrobenzophenone.**—The ketone was prepared by the method given for 4-nitrobenzophenone except that excess benzene was used as the solvent. A 76% yield of pale yellow crystals was obtained. After recrystallization from ethanol the pure compound melted at 94.7–94.9°. The literature melting point is 95°.<sup>10</sup>

**Bis-(3-Nitrobenzhydryl) Ether.**—In the preparation of 3-nitrobenzhydrol by the Meerwein–Pondorf–Verley reduction of 3-nitrobenzophenone, a light pink oil was obtained which was purified by extraction with ligroin and crystallized from ligroin one time and ethanol three times. The main product, probably the benzhydrol, was a white solid melting at 66–67° which was difficult to purify. Another product was a white crystalline material which, after recrystallization from ethanol, melted at 147.3–147.4°. The higher melting product was the bis ether as shown by a Menzies' molecular weight determination which gave a value of 432. The molecular weight is 436.4. The yield of the bis ether was about 9%. Since the bis benzhydryl ethers give the same carbonium ions as their respective benzhydrols, it was not necessary to obtain the 3-nitrobenzhydrol for this work.

*Anal.*<sup>11</sup> Calcd. for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>: C, 70.74; H, 4.57; N, 6.35. Found: C, 70.77; H, 4.46; N, 6.47.

**3,3'-Dinitrobenzophenone.**—Benzophenone was nitrated as previously described.<sup>12</sup> A 58% yield of crude compound was obtained. The highly purified compound melted at 153.4–153.8°. Literature melting points are from 148 to 155°.<sup>12–14</sup>

**3,3'-Dinitrobenzhydrol.**—The ketone was reduced by the Meerwein–Pondorf–Verley reaction using commercial aluminum isopropoxide. A 69.2% yield of crude carbinol was obtained. The highly purified material melted at 106.5–106.9°. A value of 106.8–107.6° has been reported.<sup>15</sup>

### Discussion

The decreasing ease of formation for the benzhydryl carbonium ions discussed here as well as previously<sup>3</sup> is as follows: 3-methylbenzhydryl- > benzhydryl- > 3-nitrobenzhydryl- > 4-nitrobenzhydryl- > 3,3'-dinitrobenzhydrylcarbonium ion. This order is based on the concentration of ionizing solvent, sulfuric acid, required to give visibility, which is considered to be a measure of the stability.

In general, benzhydrylcarbonium ions have absorption spectra with a principal maximum in the neighborhood of 500 m $\mu$ , and a less intense maximum around 300 m $\mu$ . Gold and Tye<sup>4</sup> state that the

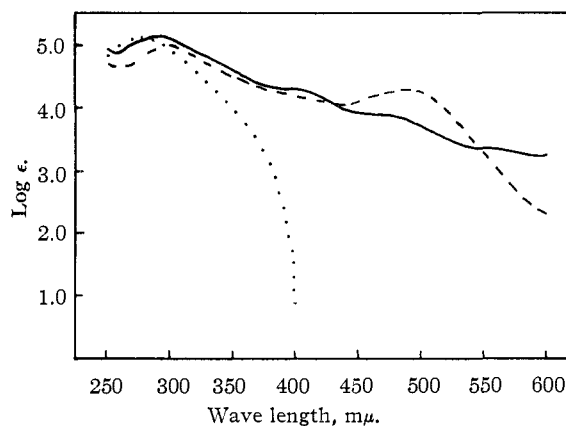


Fig. 1.—Absorption spectra of sulfuric acid solutions of: —, bis-(3-nitrobenzhydryl) ether; — — —, 4-nitrobenzhydrol; . . . . ., 3,3'-dinitrobenzhydrol.

chief variation in such spectra occurs in the intensity of this second absorption band, and that since this band is usually considerably weaker than the first one, it is probably associated with a forbidden transition, and the variation in intensity with different substituents may perhaps be associated with a varying degree of breakdown of a selection rule depending, for instance, on the deviation from planarity of the benzene rings with respect to the carbonium ion valences. For a solution made by dissolving 3-methylbenzhydrol, or benzhydrol itself, in sulfuric acid, the intensity of the first band is less than for the methyl-substituted benzhydrols which show little tendency to polymerize. For the solutions formed from bis-(3-nitrobenzhydryl) ether and 4-nitrobenzhydrol this intensity is still less, and for the dinitrobenzhydrol, the band has disappeared. However, there is still strong absorption in the region of 300 m $\mu$  for solutions of all three of the nitro-substituted compounds. If the explanation of Gold and Tye is correct, the nitro-substituents must hinder planarity of the benzene rings with the carbonium ion valences.

Deno and Schriesheim<sup>15</sup> state that 3,3'-dinitrobenzhydrol does not appear to be converted appreciably to carbonium ion in 97% sulfuric acid. The evidence presented here also indicates that there is less conversion than for any of the benzhydrols studied. The conclusion of Deno and Schriesheim was based on the fact that there is negligible light absorption in the region of 500 m $\mu$ . The spectrum of this compound reported here bears out this observation. However, the formation of polymeric materials when sulfuric acid solutions of this compound are poured into water or methanol is evidence that some ionization does occur.

Since benzhydrol, 3-methylbenzhydrol, and the three nitro compounds studied in this work readily give polymers in sulfuric acid, and since each gives an *i*-factor when the polymer is dissolved that corresponds to dimerization, with or without sulfonation depending upon the groups in the polymer structure, it is believed that the essential polymerization reaction is dimerization. Other degrees of polymerization would give *i*-factors lower than actually obtained. It is highly improbable

(8) G. Schroeter, *Ber.*, **42**, 3360 (1909).

(9) H. Lund, *ibid.*, **70**, 1520 (1937).

(10) P. J. Montagne, *Rec. trav. chim.*, **36**, 260 (1916).

(11) Analyses by Weiler and Strauss Microanalytical Laboratory, Oxford, England.

(12) E. Barnett and M. A. Mathews, *J. Chem. Soc.*, **125**, 767 (1924).

(13) L. Gattermann and H. Rudt, *Ber.*, **27**, 2296 (1894).

(14) W. Staedel, *Ann.*, **283**, 164 (1894); *Ber.*, **27**, 2111 (1894).

(15) N. C. Deno and A. Schriesheim, *THIS JOURNAL*, **77**, 3051 (1955).

that a balance between further polymerization and varying degrees of sulfonation could occur so that the integral *i*-factors would be obtained for the compounds which did polymerize. Also the molecular weight determination of the polymer formed by 4-nitrobenzhydrol in sulfuric acid is evidence for the formation of a dimer. The elemental analysis suggests that the dimer is associated with one sulfur-containing group.

It should be noted that the absorption spectra were obtained on very dilute solutions, and in the cases of the 4-nitrobenzhydrol and bis-(3-nitrobenzhydryl) ether, these were produced by extraction from a carbon tetrachloride solution as the volatile solvent was removed. Neither the concentration nor the method of preparation was com-

parable with the product isolation or "*i*"-factor experiments. The extraction method has been used quite successfully for 3-methylbenzhydrol which gives polymers in the chemical runs, and quite typical carbonium ion spectra in solutions thus prepared. This same situation is found in the titration experiments. The carbinol (or ether) was in dilute solution in carbon tetrachloride, and the first end-point obtained should be due to carbonium ions rather than polymer formation. It should be further noted that even if dimers were formed when the spectra were being obtained or during titration studies, the carbonium ions thus produced should have spectra similar to their simpler counterparts.

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## The Dipole Moments and Electronic Structures of Some Azulene Derivatives

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The dielectric constants and densities of dilute solutions of six azulene derivatives, three azaazulene derivatives, oxazulene and azaazulene in benzene have been measured and used to calculate the dipole moments of the molecules. The moment of 2-chloroazulene affords the first experimental evidence in support of the correctness of prediction by the method of molecular orbitals on the direction of moment in an azulene molecule. The analysis of the moments of 2-aminoazulene and 6-bromo-2-aminoazulene leads to the conclusion that the imino form of 2-aminoazulene, as suggested from the chemical properties of 2- and 6-amino-1,3-diazaazulenes as well as from the considerable stability of an azulonium ion, cannot be reconciled with the experimental data. The large mesomeric moment of the amino group is attributed to guanidinium-type resonance. The moments of azaazulenes, oxazulene and azaazulene can be accounted for by the probable geometric structures of these molecules with due regard to resonance contributions from highly polar structures as well as to the formation of hydrogen bonds in solutions.

Although a number of theoretical investigations<sup>1-4</sup> based on the method of molecular orbitals have been carried out on azulene and its derivatives, experimental investigations providing evidences for the conclusions thereof are still meager, probably because suitable sets of compounds of this series have not been available. Samples of eleven azulene derivatives, however, were kindly furnished by Prof. Nozoe of Tohoku University for dipole moment measurements, which enabled us to draw important conclusions concerning the electronic structures of the molecules of these compounds. The results of analysis of the measurements comprise the following scope: the experimental determination of the direction of a moment in an azulene molecule, the problem of amino-imino isomerism in aminoazulene, the mesomeric moments of Cl, Br, NH<sub>2</sub>, NHCOCH<sub>3</sub> and CN groups attached to an azulene ring, the polarity of an azaazulene molecule as well as of 1-oxazulene-2-one and 1-azaazulene-2-one molecules, and so forth.

### Experimental Method and Results

Materials, listed in Table I, were synthesized and purified in Tohoku University. The measurements were carried out at 25, 30 or 35° on dilute solutions in benzene. The dielectric constants were measured by means of a heterodyne

beat apparatus provided with a platinum cell.<sup>5</sup> The molar polarization of the solute was calculated from the experimental data by a method similar to that introduced by Halverstadt and Kumler,<sup>6</sup> differing in that densities were used rather than the specific volumes. The deformation polarizations of these deeply colored compounds were calculated from that of azulene and the contributions from various

TABLE I

	Compounds	M.p., °C.	References
1	2-Chloroazulene	91	<sup>a</sup>
2	2-Aminoazulene	93-94	<sup>b</sup>
3	6-Bromo-2-aminoazulene	135	<sup>c</sup>
4	2-Acetylaminoazulene	168	<sup>b</sup>
5	2-Cyanoazulene	78	<sup>c</sup>
6	1,3-Diethoxycarbonylazulene	125	<sup>b</sup>
7	2-Chloro-1-azaazulene	73	<sup>d</sup>
8	2,6-Dichloro-1-azaazulene	179	<sup>e</sup>
9	1,3-Diazaazulene-H <sub>2</sub> O	120	<sup>f</sup>
10	1-Oxazulene-2-one	72-73	<sup>g</sup>
11	1-Azaazulene-2-one	163-164	<sup>h</sup>

<sup>a</sup> T. Nozoe, S. Seto, S. Matsumura and T. Asano, *Proc. Japan Acad.*, **32**, 339 (1956). <sup>b</sup> T. Nozoe, S. Matsumura, Y. Murase and S. Seto, *Chem. & Ind.*, 1257 (1955). <sup>c</sup> T. Nozoe, *et al.*, to be published shortly. <sup>d</sup> T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. & Ind.*, 1357 (1954). <sup>e</sup> T. Nozoe and T. Toda, to be published shortly. <sup>f</sup> T. Nozoe, T. Mukai and I. Murata, *This Journal*, **76**, 3352 (1954). <sup>g</sup> S. Seto, *Sci. Repts. Tohoku Univ.*, **1**, 37, 367 (1953). <sup>h</sup> T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. & Ind.*, 1356 (1954).

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