

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Azulene. VIII. A Study of the Visible Absorption Spectra and Dipole Moments of Some 1- and 1,3-Substituted Azulenes^{1,2}BY ARTHUR G. ANDERSON, JR., AND BERNARD M. STECKLER³

RECEIVED MARCH 2, 1959

The shift of the principal absorption maximum in the visible region by a phenylazo group on the 1-position of azulene has been shown to be *ca.* +29 $m\mu$. Precise solution dipole moments have been obtained for azulene, 1-nitroazulene and 1,3-dihaloazulenes. On the basis of these ground state data and the dipole moment calculations of Pariser for the appropriate excited state of azulene, an explanation is advanced for the effect of different types of substituents on the visible absorption spectrum of azulene.

Introduction

The effect of alkyl substituents on the visible absorption maxima of azulene was first noted by Plattner and co-workers⁴ and subsequently used in modified form by Haagen-Smit⁵ and Pommer.⁶ Through electrophilic substitution reactions Anderson, *et al.*,⁷ obtained 1- and 1,3-substituted azulenes containing a variety of groups and extended the correlation of the shift of the principal absorption maxima with the type and number of groups present. Cowles⁸ has done a more quantitative study with respect to certain of these groups. The generalization has been made that if a substituent (on the 1-position) was less electron attracting than hydrogen, the visible absorption would be shifted to the red, and if the substituent group was more electron attracting than hydrogen, a blue shift would result.⁹

It was noted early that the haloazulenes (I) showed a red rather than the expected blue shift and subsequently it was found that the acetyl oxime group (shown in II) effected a red shift.¹⁰ The phenylazo group (shown in III) is also, in a classical sense, more electron-attracting than hydrogen and it has now been established that it

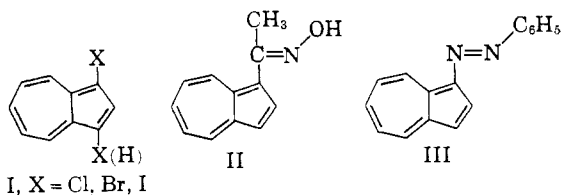
also brings about a red shift. 1-Phenylazoazulene (III) exhibits a high intensity absorption at 416 $m\mu$ (hexane) and a poorly defined maximum of low intensity at 609 $m\mu$ and this caused doubt that the shift due to this group had been assigned properly. To resolve this a number of 3-substituted 1-phenylazoazulenes were synthesized and their spectra examined. These results (Table I) plus the assignment of the peak of 416 $m\mu$ to the azo-aromatic linkage¹¹ establish the peak at 609 $m\mu$ as the maximum due to substitution by the phenylazo group.

TABLE I

VISIBLE ABSORPTION MAXIMA ($M\mu$) OF 3-SUBSTITUTED 1-PHENYLAZOAZULENES^a

Subst. group	$\Delta\lambda_{\max}^b$ (subst. group)	λ_{\max}^c (calcd.)	λ_{\max} (obs.)	Dev., %
None	609	..
-Cl	+30	639	634	0.8
-Br	+25	634	629	.8
-I	+18	627	626	.2
-NO ₂	-48	561	562	.2
-CH ₃	+30	639	633	.9

^a All spectra were taken with cyclohexane as the solvent and $\Delta\lambda_{\max}$ values are therefore different from those obtained with alcohol solutions.^{7,8} The λ_{\max} for azulene in cyclohexane was 580 $m\mu$. ^b Obtained from other substituted azulenes bearing the group indicated. ^c On basis of $\Delta\lambda_{\max}$ of +29 $m\mu$ for the phenylazo group. ^d % deviation = difference \div λ_{\max} (obs.) \times 100 to nearest 0.1.



(1) From the Ph.D. thesis of Bernard M. Steckler, University of Washington, 1957.

(2) Support for a part of this work by contracts DA-04-200-ORD-601 and DA-04-200-ORD-235 with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(3) Eastman Kodak Co. Fellow, 1956-1957.

(4) Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947); Pl. A. Plattner, A. Furst and K. Jirasek, *ibid.*, **30**, 1320 (1947).

(5) A. J. Haagen-Smit, "Fortschritte der Chemie organischer Naturstoffe," Vol. V, Julius Springer, Wien, 1948, p. 40.

(6) H. Pommer, *Ann.*, **579**, 47 (1953).

(7) A. G. Anderson, Jr., C. G. Fritz and R. Scotoni, *THIS JOURNAL*, **79**, 6511 (1957); A. G. Anderson, Jr., R. Scotoni, E. J. Cowles and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957); A. G. Anderson, Jr., J. A. Nelson and J. J. Tazuma, *THIS JOURNAL*, **75**, 4980 (1953).

(8) E. J. Cowles, *ibid.*, **79**, 1093 (1957).

(9) E. J. Cowles, Ph.D. thesis, University of Washington, 1953. This thought was also expressed in terms of the *ortho*-, *para*-directing or *meta*-directing power of the group with respect to benzene substitution. The two statements, which were used interchangeably, are actually different in that not all groups more electron attracting than hydrogen are *meta*-directing on benzene. The results of the present study are consistent with the latter statement but not with the former.

(10) C. G. Fritz, Ph.D. thesis, University of Washington, 1956.

An explanation which would account for the substituent effects of all of the different types of groups was desired, for this information was needed on the electron distribution in the azulene ring for both the ground and excited states. The former could be obtained from precise dipole moment determinations. There have been several theoretical calculations of the dipole moment of azulene,¹² but only one experimental value (1.0 ± 0.05 D.) has been reported.¹³ Although there seemed to be no reason to question the assumed direction of the azulene dipole (as shown in IV), it was intended to verify this experimentally. While the present work was in progress Kurita and Kubo¹⁴ reported the dipole moments of a number of azulene derivatives. The values ob-

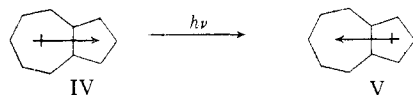
(11) Azobenzene and 1-phenylazoazulene show similar maxima at *ca.* 420 $m\mu$ in alcohol.

(12) C. A. Coulson and H. C. Longuet-Higgins, *Rev. Sci. Instr.*, **85**, 927 (1947); A. Julg, *Compt. rend.*, **239**, 1498 (1954); *J. chim. phys.*, **52**, 377 (1955).

(13) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(14) Y. Kurita and M. Kubo, *THIS JOURNAL*, **79**, 5460 (1957).

tained (e.g., 2.69 D. for 2-chloroazulene) and also our results (see below) confirm the orientation of the dipole.



Knowledge about the excited state of the azulene molecule responsible for the absorption band in the visible region was provided by the calculations of Pariser¹⁵ which gave a value of -1.36 D. for the 1B_1 state¹⁶ (represented by V) and also the charge densities for the ground and excited states. This reverse in the orientation of the dipole accompanying the transition from the ground to the excited state is most significant since it indicates a demand by the excited azulene nucleus for electrons from substituents on the five-membered ring. Thus a group possessing an inherent ability for the electromeric contribution of electrons could interact to distribute the positive charge, as shown in V and VI, and stabilize the excited state. If the substituent stabilized the ground state to a lesser extent, a decrease in the excitation energy relative to that of azulene would result and a red shift in the absorption would be observed.



To support this concept it was necessary to know the effect on the ground state of groups which caused a red shift and also of those which caused a blue shift. If the assumption is made that the change in dipole moment when a substituent is present is a measure of the stabilization (or destabilization) of the ground state, then an increase in the dipole moment associated with both types of groups would show that the group moment axis was from the azulene nucleus to the substituent for both and, therefore, that both stabilized the ground state. Consequently, an absorption shift not corresponding to the stabilization of the ground state would be due to the effect of the substituent on the excited state. Data were obtained by the careful determination of solution dipole moments of analytically pure samples of azulene, 1,3-dichloro-, 1,3-dibromo-, 1,3-diiodo- and 1-nitroazulene.¹⁷

(15) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956). A modified MO calculation with correction for configuration interaction was used. It was indicated that polar solvents would be expected to cause a blue shift in the absorption maximum relative to that obtained with non-polar solvents, presumably since the Franck-Condon principle would hold with respect to the orientation of the polar solvent molecules (which stabilize the ground state) during the photo-excitation. We have checked this on a variety of 1- and 1,3-substituted azulenes and have found it to be true in every case.

(16) W. T. Simpson, *THIS JOURNAL*, **78**, 3585 (1956).

(17) The compounds were selected to represent both types of groups (the dihaloazulenes show a red shift and the nitroazulene a blue shift) and also on the basis of ease of synthesis in the gram quantities needed, stability (1-haloazulenes are somewhat unstable oils), ease of purification and solubility in benzene (1,3-dinitroazulene is insoluble). The symmetry of the dihaloazulenes meant that the dipole moment axis and the trans-annular axis were coincident and permitted the calculation of the carbon-halogen bond moments (see Discussion).

Methods.—Dipole moments were determined by the method of Halverstaadt and Kumler.¹⁸ The equation for the solute polarization at infinite dilution as derived¹⁸ is

$$\bar{p}_{20} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + (\nu_1 + \beta) \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

The calculation was done graphically by plotting the $\epsilon_{12}-\omega_2$ and $\nu_{12}-\omega_2$ relationships. Since these were straight lines they were easily extrapolated to $\omega_2 = 0$. The intercept of the $\epsilon_{12}-\omega_2$ line gave ϵ_1 and the slope of this line gave the value of α . The intercept of the $\nu_{12}-\omega_2$ line gave ν_1 and the slope of this line gave the value of β . The solute molar polarization at infinite dilution, P_{20} , was obtained by multiplying \bar{p}_{20} by the molecular weight of the solute. P_{20} then was used to calculate the dipole moment, μ , by the equation

$$\mu = (0.01821)(10^{-18}) \sqrt{(\bar{P}_{20} - P_E)T}$$

where P_E is the electronic polarization (approximated from the molar refraction) and T is the absolute temperature (298°K.).

The difficulties associated with the calculation of the molar refractions of the highly colored solutions¹⁹ were met by the device used by the previous workers.^{13,14} In this the molar refraction of azulene was assumed to be the same as that for naphthalene, and for the derivatives the summation of the bond refractions of the appropriate atoms for the sodium D line²⁰ was added.²¹ It is felt that the assumptions implicit in this process did not result in serious errors since the dipole moments were relatively high. Also molar refractions so calculated are generally within 0.1% of the values obtained experimentally from the Lorentz-Lorentz expression and do not vary a great deal more for conjugated systems which show an exaltation of refraction.

Experimental²²

Benzene.—Reagent grade, thiophene-free benzene was shaken overnight with 15% of its volume of concentrated sulfuric acid. The separated solvent was then shaken ten times with 10% of its volume of concentrated sulfuric acid. The final acid extract was a very pale yellow. Three washings with water were followed by two washings with 10% aqueous sodium bicarbonate and then three washings with water. Following an overnight period of treatment with sodium hydride under reflux, the benzene was carefully fractionated by distillation through a 22-inch Heli-pak column; b.p. 81.1° at 760 mm., n_D^{20} 1.4979.

(18) I. F. Halverstaadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942). This method was considered to be superior to that involving a plot of total polarization against solute concentration. The notation in the equations is: subscripts 1, 2 and 12 refer to solvent, solute and solution, respectively; ϵ is the dielectric constant, d is the density, ν is the specific volume ($1/d$), ω is the weight fraction, $\alpha = \Delta\epsilon_{12}/\Delta\omega_2$, and $\beta = \Delta\nu_{12}/\Delta\omega_2$.

(19) The relationship of the refractive index to the wave length deviates from linearity and this is especially significant when the refractive index is measured in the neighborhood of a wave length where radiation is absorbed. The commonly used sodium D₁ line at 5893 Å. lies in the region of absorption (5700 to 6700 Å.) of the compounds studied. Measurements in the infrared would be more reliable, but they are very difficult to obtain.

(20) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940). A value of 1.40 for aromatic hydrogen was obtained from the Landolt-Börnstein Tables.

(21) For example, the calculation for 1,3-dichloroazulene was $P_E = R_M = C_{10}H_8 - 2(H) + 2(Cl) = 44.37 - 2(1.40) + 2(0.53) = 54.63$.

(22) Melting points were taken on a calibrated Fisher-Johns apparatus. Boiling points are uncorrected. Microanalyses were performed by B. J. Nist, C. H. Ludwig and K. Schwarz.

Nitrobenzene.—Eastman Kodak Co. white label grade nitrobenzene was steam distilled, dried over calcium chloride, and carefully fractionated by distillation through a 22-inch Heli-pak column; b.p. 210.9° at 759 mm., n_D^{25} 1.5503.

Azulene.—Azulene, prepared by a three-step modification²³ of the synthesis of Ziegler and Hafner,²⁴ was recrystallized from purified *n*-hexane; m.p. 100–100.5°, λ_{\max} (cyclohexane) 580 μ .

Anal. Calcd. for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.56; H, 6.00.

1,3-Dichloroazulene was prepared as previously described.²⁵ A total of 1.2 g. was sublimed and then recrystallized from purified *n*-hexane. The deep green needles melted at 90.0–90.5°; λ_{\max} (cyclohexane) 638 μ .

Anal. Calcd. for $C_{10}H_6Cl_2$: C, 60.95; H, 3.07. Found: C, 60.73; H, 3.18.

1,3-Dibromoazulene.—A 2.17-g. sample of this material, prepared as previously described,²⁵ was recrystallized twice from *ca.* 10 ml. of purified *n*-hexane; m.p. 90.5–91.5°, λ_{\max} (cyclohexane) 625 μ .

Anal. Calcd. for $C_{10}H_6Br_2$: C, 41.99; H, 2.12; Found: C, 42.07; H, 2.08.

1,3-Diiodoazulene.—To a magnetically stirred solution of 3.02 g. (13.4 mmole) of *N*-iodosuccinimide²⁶ in 65 ml. of dry, distilled dichloromethane was added 0.853 g. (6.65 mmole) of azulene and the flask tightly stoppered. Stirring was continued for 10 hours and the mixture poured onto a column of basic alumina. The large blue band which developed was separated readily from small yellow-orange and yellow-brown bands by elution with dichloromethane. The residue obtained by removal of the solvent *in vacuo* was chromatographed on an alumina column. A single blue band was eluted with dichloromethane–petroleum ether (1:1). Evaporation of the solvent under reduced pressure left 2.49 g. (99%) of product as a green solid. Recrystallization from benzene gave 2.25 g. (90%) of deep blue-green, feathery needles. The compound showed no melting point but changed gradually into an amorphous mass when heated above 100°. A cyclohexane solution exhibited λ_{\max} in $m\mu$ (D_{\max}) at 243 (1.35), 278 (1.21), 309 (1.73), 337 (0.18), 344 (0.24), 350 (0.28), 359 (0.41), 368 (0.26), 376 (0.54), 616 (1.25), 674 (1.1) and 752 (0.42). The material slowly decomposed to a black solid on standing in a desiccator. A chloroform solution yielded an 85% recovery of pure material after three months.

Anal. Calcd. for $C_{10}H_6I_2$: C, 31.61; H, 1.59. Found: C, 31.83; H, 1.51.

1-Nitroazulene.—The product obtained from reaction of azulene with tetranitromethane and pyridine as previously described⁷ was chromatographed twice on a column of basic alumina with dichloromethane–petroleum ether (1:1) as the eluent. Recrystallization from purified *n*-hexane and then from dichloromethane–petroleum ether gave tiny, deep red needles, m.p. 109–110°, λ_{\max} (cyclohexane) 562 μ .

1-Chloro-3-phenylazoazulene. A. From 1-Phenylazoazulene.—A mixture of 70 mg. (0.3 mmole) of 1-phenylazoazulene²⁵ and 40 mg. (0.3 mmole) of recrystallized *N*-chlorosuccinimide in 6 ml. of dry benzene was refluxed for 11 hr., at which time the solution gave a negative starch–iodide paper test. After removal of the solvent (air stream) a solution of the residue in a little dichloromethane–petroleum ether (1:10) was placed on an activated basic alumina column. Elution with dichloromethane–petroleum ether (1:20) gave a small blue fraction which showed an ultraviolet spectrum very similar to that of 1,3-dichloroazulene.²⁵ A brown-green zone and a yellow-brown zone developed but did not completely separate. The eluate containing the bulk of the former was rechromatographed three more times and then yielded 50 mg. of dark green needles. Two recrystallizations from cyclohexane gave 36 mg. (49%) of fluffy green needles, m.p. 115–116°. The ultraviolet and visible ab-

sorption of a cyclohexane solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 239 (4.36), 282 (4.32), 331 (4.27), 426 (4.46) and 634 (ϵ 655). A 10-cm. cell was employed for the region 540 to 700 $m\mu$. The infrared spectrum was recorded.

Anal. Calcd. for $C_{16}H_{11}N_2Cl$: C, 72.04; H, 4.16. Found: C, 72.03; H, 4.09.

B. From 1-Chloroazulene.—To a mixture of 72 mg. (0.44 mmole) of 1-chloroazulene, 170 mg. of sodium acetate and 10 ml. of ethanol at room temperature was added dropwise a solution of benzenediazonium chloride freshly prepared at 0° from 70 mg. (0.54 mmole) of anilinium chloride, 0.09 ml. (1.08 mmole) of concentrated hydrochloric acid, 37 mg. (0.54 mmole) of sodium nitrite and 2 ml. of water. An immediate color change to a deep brown-green was accompanied by the formation of a green solid. After standing at room temperature with occasional shaking for 10 min., the reaction mixture was washed into a separatory funnel with water and dichloromethane. The separated aqueous layer was extracted with dichloromethane three times and the combined extracts were washed once with 5% ammonium hydroxide and three times with water. Following filtration through anhydrous potassium sulfate, the organic layer was concentrated to a small volume and placed on an activated basic alumina column. A single brown-green band developed which was separated readily from a dark zone at the top with dichloromethane–petroleum ether (1:1). After concentration of the eluate (air stream) the residue was rechromatographed with a 1:5 mixture of dichloromethane–petroleum ether as the solvent. A small blue band preceded the main brown-green fraction. The latter yielded dark green crystals which after one recrystallization from cyclohexane amounted to 63 mg. (54%) of green needles identical (m.p., m.m.p., infrared spectrum) with the material obtained in A.

1-Bromo-3-phenylazoazulene.—To a solution of 25 mg. (0.108 mmole) of 1-phenylazoazulene²⁵ in 2 ml. of dry benzene was added 19.3 mg. (0.108 mmole) of recrystallized *N*-bromosuccinimide. The stoppered flask and contents were allowed to stand at room temperature overnight, at which time the solution gave a negative starch–iodide test. A second portion of *N*-bromosuccinimide was added and after 60 min. (starch–iodide test positive) the solvent was removed (air stream). The residue (dark brown with an orange-green tint) was dissolved in petroleum ether and chromatographed on an activated basic alumina column. Elution with dichloromethane–petroleum ether (1:1) effected the separation of a brown-green zone from a smaller tan band. A solution of the residue from the brown eluate fraction in petroleum ether was rechromatographed. Elution with petroleum ether separated a small blue band which was removed. The light green needles obtained by sublimation (60–70° at 1 mm.) of the residue from this fraction showed ultraviolet and visible spectra identical with those reported²⁵ for 1,3-dibromoazulene. The main band was eluted with dichloromethane–petroleum ether and the residue from this, after recrystallization from petroleum ether, gave 20 mg. (65%) of green-black needles, m.p. 114–115°. The ultraviolet and visible absorption spectra of a *n*-hexane solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 238 (4.38), 284 (4.34), 331 (4.28), 427 (4.44) and 629 (ϵ 641). A 10-cm. cell was employed for the region 540 to 700 $m\mu$. The infrared spectrum was recorded.

Anal. Calcd. for $C_{16}H_{11}N_2Br$: C, 61.75; H, 3.56. Found: C, 61.68; H, 3.76.

1-Iodo-3-phenylazoazulene.—A mixture of 50 mg. (0.216 mmole) of 1-phenylazoazulene, 48.5 mg. (0.216 mmole) of *N*-iodosuccinimide and 5 ml. of benzene was allowed to stand at room temperature for 11 days, at which time a starch–iodide test was negative (a test after 7 days was positive). A second portion of *N*-iodosuccinimide was added and, after 2 days, the mixture was freed of solvent (air stream), taken up in dichloromethane, and chromatographed on a column of activated basic alumina. Elution with dichloromethane developed a brown-green and several smaller brown bands. The former separated cleanly and was collected. The residue from this fraction was rechromatographed with 1:10 dichloromethane–petroleum ether as the eluent and the desired fraction yielded, after recrystallization from cyclohexane, 58 mg. (75%) of turquoise plates, m.p. 148.5–149.5°. A cyclohexane solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 245 (4.45), 284 (4.42), 335 (4.33), 428 (4.45) and

(23) A. G. Anderson, Jr., B. M. Steckler, D. J. Gale and R. N. McDonald, unpublished results.

(24) K. Ziegler and K. Hafner, *Angew. Chem.*, **67**, 301 (1955).

(25) A. G. Anderson, Jr., J. A. Nelson and J. J. Tazuma, *THIS JOURNAL*, **75**, 4980 (1953).

(26) C. Djerassi, *ibid.*, **75**, 3493 (1953).

(27) Identical behavior was noted by D. J. Gale (Ph.D. thesis, University of Washington, 1957) who prepared the compound by a different method.

626 (ϵ 648). A 10-cm. cell was employed for the region 545 to 695 μ . The infrared spectrum was recorded.

Anal. Calcd. for $C_{16}H_{11}N_2I$: C, 53.66; H, 3.10. Found: C, 53.67; H, 3.03.

1-Nitro-3-phenylazoazulene.—To a stirred solution of 250 mg. (1.08 mmoles) of 1-phenylazoazulene in 35 ml. of redistilled acetic anhydride was added 1.2 ml. (1.2 mmoles of acid) of a 1 *M* solution of nitric acid in acetic anhydride freshly prepared by adding 0.67 ml. of concentrated nitric acid to cold acetic anhydride and diluting with the latter to a volume of 10 ml. at 0°. Solid material separated from the initially bright red homogeneous reaction mixture but redissolved during the course of stirring for 35 hr. At this time the solution gave a negative test for 1-phenylazoazulene (a drop added to acetic acid gave a yellow-orange rather than a red color) and it was washed into a separatory funnel with 180 ml. of dichloromethane and 200 ml. of water. The aqueous layer was extracted with 30 ml. of chloroform and the combined organic layers were extracted cautiously with four 185-ml. portions of 5% aqueous sodium hydroxide. The organic solution was washed with water, filtered through anhydrous sodium sulfate, and evaporated to dryness (air stream). Chromatography of the residue on a column of basic alumina with dichloromethane-petroleum ether (1:5) developed green-yellow, maroon and orange-brown bands which were not completely distinct. Elution with the mixed solvent and then dichloromethane removed the green-yellow band which proved to be starting material. Further elution with dichloromethane removed the other two bands together and left some material, which was not investigated, remaining on the column. Rechromatography with the solvent a 1:5 mixture of dichloromethane and petroleum ether was repeated twice without achieving a separation of the maroon and orange-brown zones but did separate a small, diffuse yellow band. A third chromatogram gave a split band with the leading portion orange-red and the trailing portion orange-brown which was collected as a single fraction. Finally, chromatography on Florisil with a 1:1 dichloromethane-petroleum ether solvent effected separation of the orange-red and orange-brown fractions. The residue from the latter was subjected to sublimation at 0.1 mm. and 90° and yielded a small amount of maroon needles. These were combined with the material from the orange-red eluate and the total was 48 mg. (25% net yield), m.p. 109–110°. This material was identical (m.p., m.m.p., visible and ultraviolet spectrum) with an authentic sample of 1-nitroazulene.⁷

Anal. Calcd. for $C_{16}H_9NO_2$: C, 69.36; H, 4.08. Found: C, 69.28; H, 3.99.

The residue in the sublimator (see above) was rechromatographed over Florisil with 1:1 dichloromethane-petroleum ether as the eluent. Removal of the solvent (air stream) and recrystallization of the residue (42 mg.) from the same solvent left 32 mg. (11%) of shiny black needles, m.p. 153.5–154.5°. A cyclohexane solution showed λ_{max} in $m\mu$ ($\log \epsilon$) at 240 (4.32), 322 (4.36), 399 (4.48) and 562 (ϵ 1037). The region from 520 to 610 $m\mu$ was measured with a 10-cm. cell. The infrared spectrum was recorded.

Anal. Calcd. for $C_{16}H_{11}N_3O_2$: C, 69.30; H, 4.00. Found: C, 69.31; H, 3.82.

1-Methyl-3-phenylazoazulene.—To a suspension of 116 mg. (0.82 mmole) of freshly chromatographed 1-methylazulene and 400 mg. of sodium acetate in 8 ml. of ethanol was added a solution of benzenediazonium chloride freshly prepared at 0° from 108 mg. (0.83 mmole) of anilinium chloride, 0.2 ml. (2.4 mmoles) of concentrated hydrochloric acid, and 57 mg. (0.83 mmole) of sodium nitrite in 2 ml. of water. The reaction mixture turned deep brown immediately and was allowed to stand with occasional swirling for 10 min. It was then washed into a separatory funnel with dichloromethane and water and the aqueous layer extracted twice with dichloromethane. The combined organic solutions were washed twice with water, filtered through anhydrous sodium sulfate, and evaporated to dryness in a stream of air. The residue was taken up in a little dichloromethane-petroleum ether (1:5) and chromatographed on a column of basic alumina with the same solvent as the eluate. A small blue zone separated and was eluted. The main zone (the leading portion was yellow-brown and the trailing portion green-brown) was collected as one fraction and the residue from this placed on a Florisil column with petroleum ether. Elution with this solvent partially separated a bright red band from a larger,

trailing, deep violet one (phenylazoazulenes characteristically give reddish colors with Florisil). The yellow solution (fraction 1) corresponding to the main portion of the red zone was discarded. An intermediate eluate fraction (2) was collected (as the violet band moved down) until the eluate became green-brown. Elution was continued with petroleum ether and then dichloromethane until the eluate was colorless (fraction 3). The residue from fraction 3 was rechromatographed (Florisil). Elution with petroleum ether gave a small initial yellow-brown eluate which was discarded. The remaining material was removed with chloroform (fraction 4). Fraction 2 was rechromatographed (Florisil) with 1:20 dichloromethane-petroleum ether as the solvent. The leading red zone and a small intermediate fraction were removed and discarded. Chloroform then was used to elute the violet band and the material from this was rechromatographed (only one band formed) and combined with fraction 4. Removal of the solvent (dry air stream) and drying to constant weight (desiccator) left 159 mg. (79%) of a viscous, dark brown oil which slowly solidified over a period of several weeks, m.p. 38–48°. A cyclohexane solution showed λ_{max} in $m\mu$ ($\log \epsilon$) at 243 (4.31), 282 (4.29), 337 (4.21), 432 (4.43), 582 (ϵ 516), 612 (ϵ 511) and 633 (ϵ 508). A 10-cm. cell was used for the region from 560 to 695 $m\mu$. The infrared spectrum was recorded.

Anal. Calcd. for $C_{17}H_{14}N_2$: C, 82.89; H, 5.73. Found: C, 82.60; H, 5.91.

A trinitrobenzene derivative was prepared by treating a solution of 20 mg. (0.081 mmole) of the product in 2 ml. of ethanol with 5 ml. of a solution of trinitrobenzene in ethanol (saturated at 0°). After warming on a steam-bath for 5 min., there was obtained 20 mg. (54%) of tiny, fluffy, black needles, m.p. 163.5–164.5°.

Anal. Calcd. for $C_{22}H_{17}N_3O_6$: C, 60.13; H, 3.73. Found: C, 60.32; H, 3.76.

Apparatus.—A high precision heterodyne beat apparatus²⁸ modified for the detection of capacitance changes in the solutions was used.²⁹ The fixed capacitance circuit incorporated a thermostatically controlled quartz oscillator generating a constant frequency of 2 megacycles per second. The precision condenser used in the variable oscillator circuit was a General Radio Corporation 722 MD and was connected across the lower range (0–100 $\mu\mu\text{f}$). Ear phones and an oscilloscope were employed to detect identity in the frequencies of the differential signal and a superimposed constant reference signal of 1000 cycles per second.

The solution cell, a concentric platinum electrode vessel³⁰ with an air capacitance of 53 $\mu\mu\text{f}$., was suspended rigidly in a kerosene-bath (maintained at $25 \pm 0.03^\circ$) and attached to a train through which samples could be removed by aspiration. Solutions were prepared in 10-ml. volumetric flasks. The recording of tare, tare plus solute and tare plus solution weights permitted the calculation of the weight fraction, w , with no volumetric error.

Results.—In Table II are summarized the experimental and calculated data for the determination of the dipole moments. The error due to the assumption of the additivity of molar refractions was estimated to be less than 0.03 D. It is likely that any such error would give lower values of R_M , and thus very slightly increase the values of μ , since the exaltation factors for 1- and 1,3-substituted azulenes might be expected to be greater than those of naphthalene.³¹ In addition, the relative differences of the values of R_M for the different dihaloazulenes should not be affected appreciably by this.

The dipole moment, 4.02 D., obtained for purified nitrobenzene was identical with the average value calculated by Halverstadt and Kumler¹⁸ from the data of four previous studies. Duplicate determinations were made for azulene and the dihaloazulenes to determine the experimental error in the method. Since the determining factors in the calcu-

(28) J. Heller, Ph.D. thesis, University of Washington, 1957.

The apparatus was constructed originally by Dr. Heller for vapor phase dipole moment determinations.

(29) For details see B. M. Steckler, Ph.D. thesis, University of Washington, 1957.

(30) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 204.

(31) Optical exaltation observed with aromatic systems has been associated with the delocalization of electrons and it seems likely that there would be more electron interaction of groups on the 1-position of azulene with the aromatic nucleus than in substituted naphthalenes.

TABLE II
 DIPOLE MOMENT DETERMINATION DATA

Run	α	β	ϵ_1	ν_1	P_{30}	$\frac{P_E}{R_M} = \mu$	D.
Nitrobenzene							
	14.40	-0.320	2.273	1.1443	363.5	32.7	4.02
Azulene							
A	1.350	-0.210	2.2731	1.1447	68.23	44.37	1.08
B	1.350	-0.205	2.2734	1.1451	68.45	44.37	1.08
1,3-Dichloroazulene							
A	3.624	-0.394	2.2735	1.1446	178.4	54.6	2.46
B	3.636	-0.429	2.2732	1.1450	176.8	54.6	2.44
1,3-Dibromoazulene							
A	2.667	-0.608	2.2726	1.1447	189.2	59.4	2.52
B	2.675	-0.625	2.2730	1.1450	188.2	59.4	2.51
1,3-Diiodoazulene							
A	1.967	-0.683	2.2731	1.1446	192.8	73.5	2.41
B	1.967	-0.675	2.2730	1.1446	193.7	73.5	2.42
1-Nitroazulene							
	23.40	-0.367	2.2710	1.1446	802.9	50.9	6.06

lation were α and β , a combination of the lowest and highest values of these would provide a safe estimation of the error. This was done for each compound and the range found was ± 0.02 to 0.04 D. (Table III). The values of duplicate runs were all within 0.02 D. A plot of the data of Wheland and Mann¹⁹ by the method of Halverstadt and Kumler gave a value of 1.04 D. which, with consideration of the possible errors involved, is in good agreement with the value obtained in the present study.

 TABLE III
 DIPOLE MOMENTS (D.) AND ABSORPTION MAXIMA ($M\mu$)

Compound	μ	Est. exptl. error (D.)	λ_{\max} (cyclohexane)
Azulene	1.08	± 0.02	580
1,3-Dichloroazulene	2.45	$\pm .04$	638
1,3-Dibromoazulene	2.52	$\pm .03$	625
1,3-Diiodoazulene	2.42	$\pm .03$	616
1-Nitroazulene	6.06	$\pm .03$	532

Discussion

The dipole moments obtained show that the direction of the group moment axis is from the nucleus to the substituent(s) in each case. Thus both a halogen, which causes a blue shift, and a nitro group, which causes a red shift, apparently stabilize the ground state by the attraction of electrons. The direction of the observed spectral shifts must then be determined by the effects of the groups on the excited state. Shown in Table IV for a number of different substituents are rough energy diagrams, representing the effect of the interaction of the Kekulé structures resulting in the longest wave length absorption band. The bottom line of the split level is the energy of the ground state and the top line is the energy of the lowest excited state. Probable stabilizations for both states relative to the two arbitrary levels for azulene are qualitatively indicated. The presumed modes of stabilization and the observed spectral shift are given.

An explanation of the effect of halogen, phenylazo, acetyl oxime and similar groups is, then, that the stabilization by them of the excited state through a mesomeric electron release by the substituent is greater than the stabilization of the ground state through, primarily, an inductive electron release by the azulene nucleus. In contrast, a

 TABLE IV
 EFFECT OF SUBSTITUENTS IN 1-POSITION ON VISIBLE ABSORPTION

Substituent	Spectral shift	Mode of stabilization Ground state	Excited state	Splitting and stabilization ^a
Hydrogen	
Halogen	Bath.	Inductive	Resonance	
Phenylazo	Bath.	Inductive and resonance	Resonance	
Acetyl oxime	Bath.	Inductive and resonance	Resonance	
Alkyl	Bath. ^b	Inductive and/or hyperconj.	
Nitro	Hyps.	Inductive and resonance ^b	
Phenyl	Bath.	Resonance and inductive	Resonance	

^a The energy level diagrams are schematic only. ^b Perhaps a small inductive effect; however, see ref. 32.

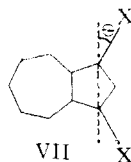
nitro group is able to stabilize markedly the ground state *via* both resonance and inductive mechanisms but has little or no ability to stabilize the excited state,³² and an increase in the excitation energy results. Alkyl and phenyl groups cause a bathochromic shift. For the former the stabilization of the excited state through an inductive and (or) hyperconjugative mechanism exceeds any small change in the ground state.³² A phenyl group is able to stabilize both states, but the effect is greater on the excited state. The six types of groups considered are representative of the substituents in any of the known 1- and 1,3-substituted azulenes.

The foregoing reasoning is consistent with the calculated values for the electron densities in the ground and excited states.¹⁵ These values, in fact, indicate that the 1-position is more electron deficient (charge density = 0.8548) in the excited state than electron rich (charge density = 1.0960) in the ground state. A certain degree of correlation of the dipole moments and spectral data for the dihaloazulenes through consideration of electronegativity differences and bond polarizabilities is possible, but there are many uncertainties involved.²⁹

Kurita and Kubo,¹⁴ in obtaining a value of 2.69 D. for 2-chloroazulene, calculated the carbon-chlorine bond moment to be 1.69 D. (the corresponding moment in chlorobenzene is 1.60 D.). The calculation was based on the assumption that the component due to the nucleus was the same as in azulene. If this assumption is made for the symmetrical 1,3-dihaloazulenes, a comparison of the carbon-halogen bond moments in these with that in the 2-chloro compound may be achieved. For a structure based on a regular heptagon and pentagon (VII), the de-

(32) In the classical sense a nitro group cannot release electrons to an electron-deficient moiety. Similarly, an alkyl group would not be able to participate in the distribution of a negative charge (in the ground state). It is possible that there could be a small degree of destabilization of the respective states by these groups.

viation of which from reality is negligible for the present purpose, the angle θ has a value of 18° .



then

$$\mu_{\text{total}} = 2 \sin \theta (\text{bond moment}_{\text{C}-\text{Cl}}) + \mu_{\text{azulene}}$$

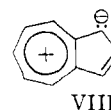
and

$$\text{bond moment}_{\text{C}-\text{Cl}} = \frac{\mu_{\text{total}} - \mu_{\text{azulene}}}{2 \sin \theta} = 2.2 \text{ D.}$$

The calculated moments for the corresponding carbon-bromine and carbon-iodine bonds are 2.3 and 2.2 D., respectively.³³ It was to be expected that

(33) A similar treatment of the unsymmetrical 1-nitroazulene cannot be made since the moment axis and the trans-annular axis are not coincident. The high dipole moment of this compound probably indicates a high moment with respect to the 1-position and the nitro group.

the carbon-chlorine bond moment would be greater in the 1-chloro- than in the 2-chloroazulene. This follows from consideration of the contribution to the ground state resonance hybrid of structures represented by VIII which provide electrons for release by induction (and resonance in the case of groups such as nitro) to the substituent. Structures having the negative charge at the 2-position are energetically less favored. The calculated ground state electron densities for the 1-position (1.0960) and the 2-position (0.9787)¹⁵ are in agreement with this interpretation.



Acknowledgments.—The authors are indebted to Prof. A. C. Huitric for generous and valuable aid in the determination of the dipole moments, and to Profs. W. M. Schubert and W. T. Simpson for their interest and helpful suggestions.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Absolute Configuration of the C₁ Atom in Retronecanone (1-Methyl-7-oxopyrrolizidine)

BY ROGER ADAMS AND D. FLEŠ

RECEIVED MARCH 11, 1959

(+)-2-Methyl-4-aminobutyric acid was converted *via* an Arndt-Eistert synthesis to (-)-3-methyl-5-aminovaleric acid which had previously been used for synthesis of (-)-retronecanone. Reduction of (-)-2-methyl-4-aminobutyric acid with lithium aluminum hydride gave (+)-2-methyl-4-amino-1-butanol. The antipode of this amino alcohol was prepared by the reduction of (-)-β-carbomethoxy-*n*-butyramide with lithium aluminum hydride. Hydrolysis of the corresponding (-)-β-carboxy-*n*-butyramide gave (-)-methylsuccinic acid. Since the absolute configuration of (-)-methylsuccinic acid is known to be S, these experiments establish the absolute configuration of the C₁ atom in (-)-retronecanone as S and hence the C₁ atom in (-)-retronecanol from which the retronecanone was prepared by oxidation as S.

Many papers and several monographs have dealt with the relative configuration of the asymmetric carbon atoms in pyrrolizidine bases.¹ Most of the structural correlations are based on the chemical interconversion and degradations of retronecine, platynecine and retronecanol. The absolute configuration of the C₁, C₂ and C₃ atoms in various natural-occurring substituted pyrrolizidines still requires clarification and a research with this objective is now under way in this Laboratory.

The conclusions of Leonard² regarding the absolute configuration of the C₁ atom in 1-methylpyrrolizidine (I)³ based on the correlation between the molecular-rotational shifts of the isoretrocanol and (-)-lupinine have been experimentally

(1) F. L. Warren, in "Progress in the Chemistry of Organic Natural Products," Vol. XI, p. 198. Springer, Wien, 1955; R. Adams and M. Gianturco, *Angew. Chem.*, **69**, 5 (1957); R. Adams, *ibid.*, **65**, 433 (1953); N. J. Leonard, in R. H. F. Manske and H. L. Holmes, "The Alkaloids," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 107.

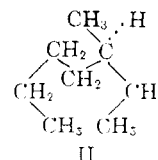
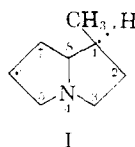
(2) N. J. Leonard, *Chemistry & Industry*, 1455 (1957).

(3) The structural formulas of the pyrrolizidine bases are drawn in such a way that the $\text{C}-\text{N}$ bond is in the plane of the paper, while the



two rings are inclined on the carbon-nitrogen axis toward each other above the plane of the paper.

tested by Warren and Klemperer.⁴ Through the appropriate degradation of heliotridane (I), they prepared (+)-3-methylheptane (II) of known absolute configuration and proved in this way that the C₁ atom of heliotridane has the S-configuration⁵ which is the opposite of that deduced by Leonard.



Adams and Leonard⁶ synthesized (-)-retrocanone (III) from (-)-3-methyl-5-aminovaleric acid (IV). The *m*-nitrobenzoyl derivative of IV was brominated in the 2-position, cyclized to the corresponding methylproline, hydrolyzed, and condensed with ethyl acrylate. The product then was subjected to a Dieckmann condensation, hydrolysis

(4) F. L. Warren and M. E. von Klemperer, *J. Chem. Soc.*, 4574 (1958).

(5) The symbolism presented in R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

(6) R. Adams and N. J. Leonard, *THIS JOURNAL*, **66**, 257 (1944).