Dipole Moments of Derivatives of 4-Phenylazo-*NN*-diethylaniline and of 9-Phenylazojulolidine (9-Phenylazo-2,3,6,7-tetrahydro-1*H*,5*H*-benzo-[*ij*]quinolizine)

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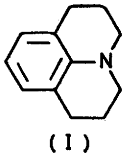
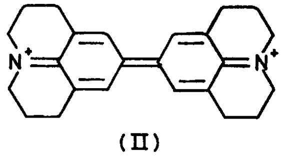
Apparent dipole moments in benzene of a series of *para*-substituted derivatives of 9-phenylazojulolidine (9-phenylazo-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine) have been determined together with those of the corresponding series derived from 4-phenylazo-*NN*-diethylaniline. Vector moments, μ(int), in the direction of the major axis of the molecules have been calculated in order to explain the observed moments. The values of μ(int) for the 9-phenylazojulolidines are all greater than those for the corresponding 4-phenylazo-*NN*-diethylanilines and, for both series of compounds, increase with increase in the Hammett substituent parameter, σ_p. Evidence is presented that the terminal nitrogen atom is more nearly planar in the 9-phenylazojulolidines than in the 4-phenylazo-*NN*-diethylanilines and also that μ(int) arises by interaction of the *para*-substituent with the π-electron distribution in the aromatic ring to which it is attached.

ESSENTIALLY strain-free models (Dreiding) of julolidine (2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine) (I) containing either sp^2- or sp^3-hybridised nitrogen can be constructed, but the sp^2-hybrid permits more efficient conjugation with the aromatic nucleus. It is usually accepted that the nitrogen atom in *NN*-dimethylaniline is sp^3-hybridised,[1] and it may be that the reduced intensity of the second band in the electronic absorption spectra of julolidine compared with that of *NN*-dimethylaniline implies a different state of hybridisation.[2] In support of this explanation, it is noted that julolidine reacts with nitrous acid to produce a quinonoid structure (II).[3] Also, the dijulolidyl ketone (III) exhibits a marked tendency to form the quinonoid cation (IV) in acid solution.[2]


(I)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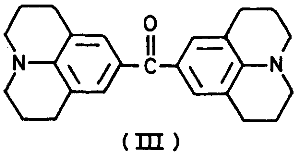
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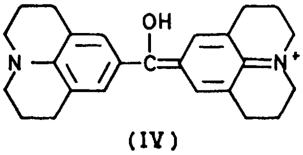
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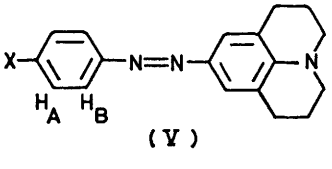
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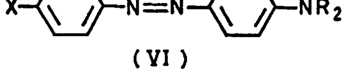
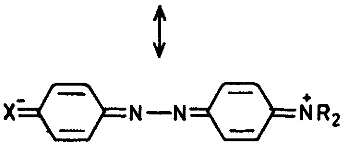

(VI)


(VII)

The electronic spectra of a series of *para*-substituted derivatives of 9-phenylazojulolidine (V)[4] and a corresponding series derived from 4-dialkylaminoazobenzene (VI) have been recorded.[5] The bathochromic shifts of the first band of the former series relative to those of the corresponding derivatives of the latter series are much greater (*ca.* 40 nm) than calculated.[4] This finding was partly attributed[4] to improved π-interaction of the amino-nitrogen atom with the aromatic ring brought about by the methylene bridges in the julolidine ring system.

Further evidence for a change towards a more sp^2-state of hybridisation of the nitrogen atom in 9-phenylazojulolidine, and hence in julolidine itself, is provided by the results of the present study of the dipole moments of a series of *para*-substituted derivatives of 4-phenylazo-*NN*-diethylaniline and the analogous compounds derived from 9-phenylazojulolidine.

EXPERIMENTAL

The apparent dipole moments were calculated as described previously[6] from experimental measurements at 25.0 °C of permittivity, specific volume, and refractive index to Na$_D$ radiation [listed in Supplementary Publication No. SUP 23097 (14 pp.) †] of a series of dilute solutions of graded concentrations of each solute in benzene. The slopes α, β,

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

and ν, respectively, of the linear graphs of permittivity, specific volume, and refractive index squared against weight fraction, together with polarisation data, in which the symbols have their usual significance, and the computed dipole moments, μ, are given in Tables 1 and 2.

Materials.—Benzene was purified as previously.[7] The solutes, which gave satisfactory microanalytical data and n.m.r. spectra, were purified immediately prior to use. Most of the azo-dyes derived from julolidine have been described earlier.[4] 4-Diethylaminoazobenzene [8] and its *p*-bromo,[8] *p*-chloro,[8] *p*-fluoro,[9] *p*-iodo,[8] *p*-methyl,[8] *p*-cyano,[10] and *p*-nitro [8] derivatives were prepared by standard procedures and the pure dyes gave m.p.s in agreement with the values recorded in the literature.

TABLE 1

Polarisation data and dipole moments, μ, at 298 K for solutions in benzene of a series of julolidine and 9-phenylazojulolidine derivatives

9-Substituent in julolidine	α	β	ν	$P_{2,\infty}$/cm^3	$_EP_2$/cm^3	μ/D
H	2.163	−0.227	0.276	117.85	55.69	1.74 (±0.01)
Me	1.340	−0.194	0.195	100.24	58.85	1.42 (±0.01)
para-Substituent in 9-phenylazojulolidine						
H	5.903	−0.302	0.923	376.26	117.16	3.57 (±0.02)
Me	4.279	−0.328	0.956	305.04	122.65	2.99 (±0.03)
F	10.344	−0.394	0.833	640.00	111.74	5.08 (±0.03)
Cl	10.692	−0.368	1.027	698.77	131.89	5.14 (±0.03)
Br	9.447	−0.416	0.961	709.62	141.26	5.27 (±0.03)
I	8.043	−0.485	0.684	688.56	130.44	5.23 (±0.04)
CF_3	15.359	−0.424	0.728	1 070.93	120.75	6.82 (±0.04)
CN	26.929	−0.331	1.456	1 602.06	155.83	8.41 (±0.02)
NO_2	26.452	−0.489	0.993	1 664.55	122.84	8.68 (±0.02)
COMe	14.759	−0.391	1.141	956.59	139.79	6.32 (±0.03)
OMe	3.914	−0.328	0.743	300.57	116.95	3.00 (±0.03)

TABLE 2

Polarisation data and dipole moments, μ, at 298 K for solutions in benzene of a series of *NN*-diethylaniline and 4-phenylazo-*NN*-diethylaniline derivatives

4-Substituent in *NN*-diethylaniline	α	β	ν	$P_{2,\infty}$/cm^3	$_EP_2$/cm^3	μ/D
H	2.466	−0.072	0.123	116.08	50.39	1.80 (±0.01)
Me	1.546	−0.033	0.096	101.50	56.17	1.49 (±0.01)
para-Substituent in 4-phenylazo-*NN*-diethylaniline						
H	5.798	−0.219	0.851	346.43	109.86	3.40 (±0.02)
Me	4.168	−0.202	0.826	284.91	115.83	2.88 (±0.03)
F	10.027	−0.273	0.744	582.51	107.82	4.82 (±0.02)
Cl	10.326	−0.260	0.858	635.63	121.73	5.01 (±0.04)
Br	9.458	−0.382	0.813	667.29	125.71	5.15 (±0.02)
I	7.999	−0.471	0.828	646.87	134.73	5.01 (±0.03)
CF_3	14.668	−0.338	0.692	965.37	118.33	6.44 (±0.02)
CN	27.183	−0.232	1.154	1 500.54	135.70	8.17 (±0.04)
NO_2	27.134	−0.276	1.267	1 602.31	148.04	8.43 (±0.04)

9-(4-*Acetylphenylazo*)*julolidine*, m.p. 188—189 °C, was obtained by coupling 4-acetylbenzenediazonium chloride with julolidine in buffered aqueous acetic acid. The crude product was purified by column chromatography and crystallised from ethanol (Found: C, 75.4; H, 6.8; N, 13.0. $C_{20}H_{21}N_3O$ requires C, 75.2; H, 6.6; N, 13.2%).

9-(4-*Cyanophenylazo*)*julolidine*, m.p. 187—188 °C, was obtained in a similar manner from 4-cyanobenzenediazonium chloride and julolidine (Found: C, 75.7; H, 6.0; N, 18.4. $C_{19}H_{18}N_4$ requires C, 75.5; H, 6.0; N, 18.5%).

p-*Trifluoromethyl*-4-*diethylaminoazobenzene*, m.p. 107 °C, was prepared from diazotised 4-trifluoromethylaniline and *NN*-diethylaniline (Found: C, 63.8; H, 5.9; F, 17.6; N, 12.9. $C_{17}H_{18}F_3N_3$ requires C, 63.5; H, 5.7; F, 17.7; N, 13.1%).

DISCUSSION

If the configuration at the nitrogen atom in 9-phenylazojulolidine and its *para*-derivatives is more nearly planar than that in the corresponding derivatives of diethylaminoazobenzene, it can be anticipated that the additional moments, in the direction of the major axis of the molecules, necessary to explain the observed dipole moments will be greater in the former series of compounds than in the latter. Thus, these additional moments, regarded as interaction moments, μ(int), have been calculated vectorially and their values are recorded in Table 3.

Although *trans*-azobenzene is not quite planar even in the crystalline state, it is assumed for the purpose of the calculation that the major axes of the ring moieties Y and Z in the azo-molecule Y−N=N−Z are parallel. The angles which the functional group moments make with the directions of the major axis of julolidine and *NN*-diethylaniline (26° 55′ and 29° 43′, respectively) are obtained by combining separately the observed moments of julolidine (1.74 D) and *NN*-diethylaniline (1.80 D) with the moment of toluene (0.37 D) to give the observed moments of 9-methyljulolidine (1.42 D) and 4-methyl-*NN*-diethylaniline (1.49 D). Taking dipole moments[11] of fluoro-, chloro-, bromo-, iodo-, trifluoromethyl-, cyano-, and nitro-benzene as 1.48, 1.58, 1.56, 1.40, 2.56, 4.03, and 4.01 D, respectively, and using the above angles permits the values of μ(int) to be calculated by applying the cosine rule.

TABLE 3

Calculated μ(int) values necessary to explain the observed dipole moments of the *para*-derivatives of 9-phenylazojulolidine and of 4-phenylazo-*NN*-diethylaniline

		μ(int)		
Substituent	σ_p	(V)	(VI)	$\Delta\mu$(int)
Me	-0.17	1.70	1.55	0.15
H	0	1.93	1.72	0.21
F	0.06	1.99	1.69	0.30
Cl	0.24	1.95	1.79	0.16
Br	0.27	2.10	1.95	0.15
I	0.28	2.22	1.97	0.25
CF_3	0.54	2.66	2.25	0.41
CN	1.00 [a]	2.79	2.53	0.26
NO_2	1.27 [a]	3.08	2.81	0.27

[a] Enhanced values of σ_p appropriate to anilines (J. Miller and A. J. Parker, *Aust. J. Chem.*, 1958, **11**, 302).

From the data in Table 3, it is seen that the values of μ(int) for the 9-phenylazojulolidine derivatives are greater than the corresponding values for the 4-phenylazo-*NN*-diethylaniline analogues. It is also noted that μ(int) increases with increase in the Hammett substituent parameter, σ_p, in both series of compounds, but no consistent trend in the differences between μ(int) for the two series, $\Delta\mu$(int), is observed. These observations are interesting when reference is made to the work of Hallas,[12] who previously reported that the chemical shifts of the protons in the julolidine moiety of the *para*-substituted derivatives of 9-phenylazojulolidine (V) remain virtually unaffected by changes in the substituent X. However, the chemical shift of H_A varies and a linear relationship between $\Delta\tau(H_A - H_B)$ and σ_p is noted. It is likely that the terminal nitrogen atom in 9-phenylazojulolidine interacts more strongly with the delocalised system to which it is attached than does that of 4-phenylazo-*NN*-diethylaniline (VI). This delocalisation increases the π-electron density at the phenylazo-group so that μ(int) and n.m.r. data reflect the extent to which this electronic distribution is perturbed by the *para*-substituent. In explanation, the authors conclude that the terminal nitrogen atom in the 9-phenylazojulolidines is more nearly sp^2-hybridised than that in the 4-phenylazo-*NN*-diethylanilines.*

In order to establish that the conformation at the terminal nitrogen atom is more nearly planar in the julolidine compounds than in the diethylaniline derivatives, and that the hybridisation is influenced by strongly electron withdrawing substituents, an *X*-ray crystallographic analysis would be useful.

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* A referee suggests that the experimental results could be explained if the 9-phenylazojulolidines are more nearly planar in solution than the 4-phenylazo-*NN*-diethylanilines.