THE MOLAR REFRACTION OF DI-AROMATIC SYSTEMS

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The molar refraction of four di-aromatics is determined. The values obtained indicate that the mobility of the π-electrons is restricted to each individual aromatic unit. This is confirmed by determination of the u.-v. spectra.

In a previous publication [1] a method of calculating the molar refraction of condensed aromatic compounds was discussed. It is based on the assumption that the highly mobile π-electrons can follow the rapidly oscillating electromagnetic field without relaxation.

The method was verified by calculations on a number of aromatic substances with condensed rings, including compounds with five-membered rings (like fluorene) and with two aromatic parts joined by a bond between two such rings (difluorenyl).

The difference between the molar refraction R_M and the sum of the atom refractions R'_M was called the molar refractometric increment, I_M:

$$I_M = R_M - R'_M.$$

The absolute value of the refractometric increment per aromatic carbon atom appeared to be a measure of the size of the aromatic ring cluster.

Thence, it was shown that in compounds like fluorene, benzfluorene and fluoranthene the value of I_M is such that mobility of the π-electrons must be assumed to exist throughout the aromatic ring-system. This would be expected from theory since the whole ring-system in these compounds is almost planar.

It seemed interesting to check whether in di-aromatics this mobility of the π-electrons is limited to each aromatic unit, or whether some interaction between the π-electrons of each unit would take place.

As could be expected from the non-planarity of the aromatic rings, no such interaction occurs; and the experimentally determined values for the molar refraction of diphenyl, 1,1′-dinaphthyl, 9,9′-dianthryl and 9,9′-diphenanthryl prove to be in good agreement with that calculated by multiplying the contribution of each separate aromatic unit (i.e. phenyl, naphthyl, anthryl and phenanthryl) by two. The results are shown in table 1.

TABLE 1.—COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

compound	solvent	% by weight	R_M expt.	S^* (Å^2)	R_M calc.	$R'_M = \sum \nu_i R_i$	I_M expt.	I_M calc.
diphenyl	xylene	2·80	52	29·5	50	41	11	9
1,1′dinaphthyl	,,	0·95	85	49·2	84	66	19	18
9,9′dianthryl	,,	0·92	123	68·9	122	91	32	31
9,9′diphenanthryl (solution)	,,	0·86	121	68·9	122	91	30	31
9,9′diphenanthryl (liquid)	d_4^{20} 1·187	n_D^{20} 1·78	125	68·9	122	91	34	31

Finally, the ultra-violet spectra of dinaphthyl, dianthryl and diphenanthryl, determined in this laboratory by Mr. Groenewege, were found to be identical with those of 1-methylnaphthalene, 9-methylanthracene and 9-methylphenanthrene respectively. This confirms the single-bond character of the link between the aromatic units.

EXPERIMENTAL

The determination of the molar refractions (R_M measured using the Lorentz-Lorenz formula) was carried out by measuring at 20° the density and the refractive index (Na D line, 5 readings) of a solution in xylene and determining from these data the molar refraction of the respective solution (R_M solution). From this value the molar refraction of the dissolved compound is derived using the equation,

$$R_M \text{ (solution)} = \gamma \text{ (solvent)} R_M \text{ (solvent)} + \gamma \text{ (compound) } R_M \text{ (compound)}, \qquad (1)$$

where γ is the molar fraction of solvent and compound respectively.

The accuracy of this method is not great, as, first, the applicability of formula (1) may be limited by interaction between solvent and solute and, secondly, small inaccuracies in the refractive indices and densities of solution and solvent may give rise to serious errors (the solubility of the compounds in xylene is low).

With 9,9′-diphenanthryl the accuracy could be checked, as it was observed that, on cooling, molten 9,9′-diphenanthryl turned into a super-cooled liquid from which the crystalline modification could be reobtained by dissolving it in chloroform and adding ethanol to the solution. Determination of the refractive index from the reflectance [2] and direct determination of the density of this liquid form yielded a value of 125 for the molar refraction of 9,9′-diphenanthryl. This value is in fair agreement with that obtained by the solution method (121).

Comparison with the molar refraction of diphenyl as calculated from literature data shows a fair agreement. Using $n_D^{20} = 1{\cdot}614$ [8] and the density of liquid diphenyl extrapolated to 20°C ($d_4^{20} = 1{\cdot}041$),[8] a value of 51·5 is obtained.

The calculated molar refractions (R_M calc.) are obtained by means of eqn. (2):

$$R_M = \underbrace{F(S^*)}_{\substack{\text{contribution from}\\ \text{the aromatic part}\\ \text{of the molecule}}} + \underbrace{[R'_M - C_a R_c]}_{\substack{\text{contribution from the}\\ \text{aliphatic part of the}\\ \text{molecule}}}, \qquad (2)$$

where C_a = number of aromatic carbon atoms,†

R_C = atomic refraction of carbon,

$R'_M = \Sigma \nu_i R_i = \nu_H R_H + \nu_C R_C$,

and $F(S^*)$ is determined from S^*‡ using the graph on p. 1393 of the previous publication.[1]

For R_C and R_H the values of the atom refractions given by Wibaut and Langedÿk [3] are used: $R_C = 2{\cdot}558$ cm³, $R_H = 1{\cdot}039$ cm³.

The aromatic area S^* was determined by a modified procedure [4] using the formula $S^* = C_a S^*_C$, which is based on the assumption that the area is limited to the aromatic *carbon* atoms only. Using benzene as a model substance, a value of 2·46 Å² is found for S^*_C, the area of each aromatic carbon atom.

SUBSTANCES EXAMINED

diphenyl	commercial product, m.p. 70·0-70·2° (lit. 69-71°);
1,1′-dinaphthyl	prepared according to Sakellarios and Kyrimis,[5] m.p. 153·5-153·9° (lit. 154°);

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† In these cases $\nu_C = C_a$, but formula (2) as given above can also be used for substituted (di)-aromatics.

‡ For a definition of S^*, cf. (4).

9,9′-diphenanthryl	prepared according to Bachmann,[6] m.p. 187·1-187·6° (lit. 184-185°);
9,9′-dianthryl	synthesized by reduction of anthrone in glacial acetic acid with zinc and hydrochloric acid at reflux. Yield 85 %; m.p. 317·0-317·4° (lit. 308° [7]). Analysis C 94·7, H 5·2 (calc. C 94·9; H 5·1).

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[6] Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363.
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