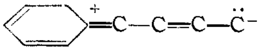
the *trans* may be due to the configurational difference.

The *cis* isomers of most olefins and of piperylene have higher values for the boiling point, refractive index, and density than the *trans* isomers. For the phenylbutadienes the opposite order has been found. Steric inhibition of resonance is a possible factor in determining the lower refractive index and molar refraction for *cis*-phenylbutadiene. Contributing forms in which there is a double bond between the ring and the *alpha* carbon atom, *e.g.*,



require a coplanar arrangement of the ring and side chain. In the *cis* configuration the phenyl and vinyl groups are too bulky, as shown by molecular models, to allow coplanarity, with the result that the contributions of such structures is reduced. It seems reasonable that this restriction on electron mobility (*i.e.*, reduced polarizability) would be reflected in a lower refractive index, molar refraction and boiling point.

Another consequence of this inhibition of resonance and reduced coplanarity is the decrease in wave length of maximum absorption and the degree of absorption in the ultraviolet region, as has already been demonstrated in the case of ortho-substituted benzoic acids,[24] benzils[25] and ortho and alpha substituted styrenes.[26]

Acknowledgment.—The authors wish to thank the du Pont Company for a fellowship, 1948–1949, E. C. Hughes and R. C. Foreman of the Standard Oil Company of Ohio for the infrared spectra, and L. C. Gibbons and J. F. Thompson of the N.A.C.A. Laboratory, Cleveland, for the freezing point determinations.

[24] Ross, THIS JOURNAL, **70**, 439 (1948).

[25] Leonard and Blout, *ibid.*, **72**, 484 (1950).

[26] Hirschberg, *ibid.*, **71**, 3241 (1949).

CLEVELAND, OHIO RECEIVED MAY 29, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Diamagnetic Anisotropy of Polyethylene, Polystyrene and Poly-2,5-dichlorostyrene

BY ELIZABETH M. WEIR[1] AND P. W. SELWOOD[2]

Measurements of diamagnetic anisotropy have been made on polyethylene, polystyrene and poly-2,5-dichlorostyrene. The samples used were in the form of fibers in several stages of elongation. Measurements were made by the Krishnan flip method. Calculations have been made of the anisotropy to be expected for several molecular orientations. Orientations of the aromatic groups in the two polystyrenes have been computed from the experimental data. Stretched polyethylene shows an almost negligible anisotropy, stretched polystyrene shows a small anisotropy and stretched poly-2,5-dichlorostyrene shows a large anisotropy. A few measurements of average (powder) susceptibilities have been made by the Faraday method.

A diamagnetic substance is one in which the magnetic flux density within the substance is less than in an impressed field surrounding it. The magnitude of the diamagnetism depends upon the average effective radius of the electronic orbits of the individual atoms. When the arrangement of the atoms in a substance is such that the average electronic radius is not the same in all directions in space, the substance has different magnetic susceptibilities along different directions and is therefore magnetically anisotropic. A completely amorphous high polymer will be magnetically isotropic, but as soon as it becomes oriented it will be anisotropic. An undrawn polymer fiber is nearly isotropic but, as the fiber is drawn, the orientation increases and the anisotropy becomes greater. The effect is especially noticeable in polymers containing aromatic groups because aromatic rings have a large magnetic anisotropy. Measurements of diamagnetic anisotropy are thus of use in determination of molecular orientation in certain classes of high polymers.

Experimental Part

Preparation of Samples.—Description, source and preparation of the several high polymer samples were: Polyethylene "unoriented monofilament"[3] was cut from the original coil into cylindrical rods about 8 mm. long and 1 mm. in diameter. The long axis of the samples was the long axis of the original material.

Polyethylene "monofilament machine stretched 249%"[3] was cut in rods, three or four of which were fastened together to form a bundle. The long axis of the sample was in the direction of stretching.

Polyethylene "partially drawn 280% elongation"[4] was cut from much longer rods. The long axis of the samples was in the direction of stretching.

Polyethylene "fully drawn 520% elongation"[4] was similarly cut from long rods. The long axis was in the direction of stretching.

Polyethylene "monofilament machine-stretched 574%"[3] was in the form of filaments which were wound several times around a frame, then tied and cut off in bundles 6 to 8 mm. long. Again the long axis was in the direction of stretching.

Polystyrene "unoriented monofilament"[4] was in the form of brittle cylindrical rods. Short sections about 5 mm. long were cut off with a razor blade. The long axis of the sample was the long axis of the original rod.

Polystyrene "monofilament machine-stretched 980%"[4] was made into fiber bundles large enough for measurement. The long axis of the bundles was in the direction of stretching.

Poly-2,5-dichlorostyrene "drawn about 500%"[4] was in the form of bars a few cm. long and with a cross-section of 2–3 mm.[2] Samples were cut 6 or 7 mm. long. The long axis was in the direction of stretching. It should be mentioned that the use of a razor blade to cut hard material often introduces a minute but extremely undesirable trace of strongly ferromagnetic steel. Careful washing of samples generally removes this difficulty.

Magnetic Anisotropy Measurements.—These were made by the Krishnan second, flip-angle, method.[5] Details of the

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[1] The award of the du Pont Company Postgraduate Fellowship in Chemistry is gratefully acknowledged.

[2] Inquiries concerning this paper should be addressed to P. W. Selwood.

[3] Supplied by the Bakelite Division, Union Carbide and Carbon Corporation, through the courtesy of Dr. V. E. Meharg.

[4] Supplied by the Bell Telephone Laboratories through the courtesy of Dr. W. O. Baker.

[5] K. S. Krishnan, B. C. Guha and S. Banerjee, *Phil. Trans. Roy. Soc. (London)*, **A231**, 235 (1933); **A234**, 265 (1935).

measurements as applied to polymer fibers have previously been described from this Laboratory.[6] All magnetic measurements were made at room temperature.

Susceptibility Measurements.—These were made on a Faraday balance.[7]

Results

The magnetic anisotropy data given in Table I are the averages of several determinations on at least four samples of each polymer studied. Individual readings differ quite widely owing to accidental effects and to considerable inhomogeneity in the various samples. In Table I the orientation given is the angle made by the long axis of the sample with the direction of the field, in the plane perpendicular to the axis of suspension. Thus an orientation angle of 90° means that the sample tended to turn at right angles to the field and that the larger diamagnetic principal susceptibility (minimum algebraic susceptibility) lies along the long axis of the sample. It will be noted that for most of the stretched polymers this maximum diamagnetism is in the direction of stretching. This is in contrast to the case of polyethylene terephthalate previously reported from this Laboratory.[6] In Table I the anisotropies are given per repeating unit. For the polyethylenes the repeating unit is considered to be the ethylene group.

TABLE I

MOLECULAR DIAMAGNETIC ANISTROPY OF POLYMERS (PER REPEATING UNIT × 10^6)

Sample	Elongation, %	Orientation, degrees	Anisotropy
Polyethylene	None	0	2.2
Polyethylene	249	30	2.4
Polyethylene	280	90	0.8
Polyethylene	520	90	1.2
Polyethylene	574	0	2.8
Polystyrene	None	45	0.8
Polystyrene	980	90	5.3
Poly-2,5-dichlorostyrene	~500	90	22.3

The average susceptibility of powdered poly-2,5-dichlorostyrene was found in two independent tests to be -105 and -99.6 ($\times 10^{-6}$), for an average of -102×10^{-6} per repeating unit.[8]

Calculation of Magnetic Anisotropy in Polystyrene and Poly-2,5-dichlorostyrene.—All the polymer fibers resemble uniaxial crystals. They possess only two principal susceptibilities—one along the length of the fiber, the other perpendicular to the unique axis. Both polystyrenes orient perpendicular to the magnetic field and, therefore, must have the larger diamagnetic susceptibility along the fiber axis. Since the largest contribution to the magnetic anisotropy is made by the aromatic groups, and since the largest diamagnetic susceptibility in aromatic groups is perpendicular to the plane of the rings, it follows that the aromatic groups in both styrenes have a preferred orientation such that the plane of the rings tends to be perpendicular to the fiber axis, and the normal to the plane of each of these rings tends to be parallel to the fiber axis.

It may be seen from molecular models that the aromatic rings must lie perpendicular, or nearly so, to the long axis of the polymer chain in both polystyrenes. But the second condition for a maximum anisotropy, that the normal to the plane of each ring should be parallel to the chain axis, is not necessarily fulfilled. In polystyrene it appears that the rings may rotate around the carbon–carbon bond with something less than free rotation. In the poly-2,5-dichlorostyrene this rotation about the carbon–carbon bond joining the ring to the chain will be much less because the chlorine atom in the 2-position restricts rotation to a few degrees on either side of the perpendicular position.

A second point to be considered is the twisting of the chain and the distribution of aromatic rings around the chain. In the unstretched polymer kinking of the chain should lead to random orientation of the rings with respect to any given direction in the polymer mass. Thus the anisotropy of the unstretched polymer should be negligible and comparable in that respect to the anisotropy of unstretched polyethylene. When the polystyrenes are stretched the uncoiling of the chains will result in a small anisotropy comparable in magnitude to that of stretched polyethylene, plus the anistropy contribution of oriented aromatic rings. For stretched polystyrene the contribution of the aromatic groups may not be very large; for stretched poly-2,5-dichlorostyrene the contribution of the aromatic groups may be substantial.

The following calculation will give the maximum magnetic anisotropy to be expected if all aromatic groups are oriented with the normal to the plane of the rings strictly parallel to the fiber axis. This will be done for unstretched polystyrene (an improbable case), for stretched polystyrene, and for stretched poly-2,5-dichlorostyrene. The polystyrenes are considered as polyethylene chains with aromatic groups substituted for hydrogen atoms at regular intervals. The repeating unit is regarded as the repeating unit in polyethylene minus one hydrogen atom but plus a phenyl group or a 2,5-dichlorophenyl group. In other words, the fragments to be considered are $-CH-CH_2-$, $-C_6H_5$ and $-C_6H_3Cl_2$.

The average molecular susceptibility of the polyethylene fragment, $-C_2H_4-$, is $\bar{K}$ which is equal to the average molar susceptibility χ. This may be estimated from Pascal's constants to be -23.72.[9] From this there is subtracted the molar susceptibility of one hydrogen atom, which is assumed to be magnetically isotropic. Hence the $\bar{\chi} = \bar{K} = -23.72 + 2.93 = -20.79$ per C_2H_3 group. To obtain the effective principal molecular susceptibilities of this group we shall use the observed anisotropies reported in Table I. This involves two minor difficulties. The first is that the percentage elongation for polystyrene went up to 980%, while the highest elongation for any polyethylene was 574%. The method used to overcome this difficulty is to extrapolate the measured polyethylene anisotropies to 980% elongation. This questionable procedure is justifiable under the circumstances because the polyethylene anisotropies are so small

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(6) P. W. Selwood, John A. Parodi and Anderson Pace, Jr., THIS JOURNAL, **72**, 1269 (1950).

(7) To be described later.

(8) The authors are indebted to Mr. P. E. Jacobson for assistance in this and other measurements on the Faraday balance.

(9) From this point all susceptibilites are given in units of 10^{-6}.

that the error introduced into the final result for the polystyrenes will be only about one unit. The second difficulty is a little more serious. Some of the polyethylenes gave an orientation in the magnetic field of 0° and others of 90°. We are inclined to attribute the 0° orientation to accidental impurities because both Ramanadhan and Lonsdale[10] have shown that long chain organic compounds containing no aromatic groups and few or no multiple bonds show a maximum diamagnetism parallel to the long axis of the molecule. Writing $(2K_1 + K_3)/3 = \bar{K} = -20.79$ and $K_3 - K_1 = \Delta K = \Delta\chi$, we have $K_1 = -20.79 + \Delta\chi/3$. The results are summarized in Table II where K_1 and K_3 are effective principal susceptibilities of the C_2H_3 group across and along the C–C bond, respectively.

TABLE II

EFFECTIVE PRINCIPAL SUSCEPTIBILITIES OF THE POLYETHYLENE FRAGMENT AT SEVERAL ELONGATIONS ($\times 10^6$ PER C_2H_3 GROUP)

Elongation, %	$-K_1$	$-K_2$
None (Extrptd.)	20.63	21.13
280	20.56	21.34
520	20.42	21.52
980 (Extrptd.)	20.21	21.96

The principal molecular susceptibilities for the phenyl group may be found from Krishnan's[5] data on benzene, for which $K_1 = K_2 = -38.3$ per mole, and $K_3 = -91.2$ per mole, where K_1 and K_2 are the principal molecular susceptibilities in the plane of the ring and K_3 is the susceptibility perpendicular to the ring. Correction for one magnetically isotropic hydrogen atom gives $K_1 = K_2 = -34.4$ per mole and $K_3 = -88.3$ per mole for the phenyl group.

In a similar manner the principal molecular susceptibilities for the 2,5-dichlorophenyl group are calculated from Krishnan's value for the average molecular susceptibility of paradichlorobenzene, and the known principal molecular susceptibilities of benzene. Thus, for the C_6H_3 fragment

$$K_1 = K_2 = -37.3 + (3 \times 2.93) = -28.5$$
$$K_3 = -91.2 + (3 \times 2.93) = -82.4$$
$$\bar{K} = (-28.5 - 28.5 - 82.4)/3 = -46.5$$

According to Krishnan $\bar{K}$ for paradichlorobenzene is -85.3. Correction for one hydrogen atom gives $\bar{K} = -82.4$ for the $C_6H_3Cl_2$ group. Hence the contribution of two isotropic chlorine atoms must be $-82.4 + 46.5 = -35.9$. This should be added to each principal molecular susceptibility for C_6H_3, giving for $C_6H_3Cl_2$

$$K_1 = K_2 = -28.5 - 35.9 = -64.4$$
$$K_3 = -82.5 - 35.9 = -118.3$$

We shall now compute the maximum anisotropy to be expected for the three polymers. The first is unstretched polystyrene for which it will be assumed that the chains are arranged at random or nearly so but through some imaginary force the aromatic groups are arranged so that the normals to their planes are all parallel. The principal molecular susceptibility in this preferred direction will then be the sum of K_3 for the C_2H_3 group plus K_3 the largest diamagnetic susceptibility for the phenyl group. That is

$$K_{\parallel} = \chi_{\parallel} = K_3(C_2H_3) + K_3(C_6H_5) = -21.1 + -88.3 = -109.4$$

The principal susceptibility at right angles to the preferred direction will be

$$K_{\perp} = \chi_{\perp} = K_1(C_2H_3) + K_1(C_6H_5) = -20.6 - 34.4 = -55.0$$

Hence the maximum anisotropy for unstretched polystyrene is

$$\chi_{\parallel} - \chi_{\perp} = -109.4 + 55.0 = -54.4 \text{ per repeating unit}$$

The second polymer for which a similar calculation will be made is the polystyrene stretched to 980%. The only difference in the computation is that here the chains are assumed to be strongly oriented, hence we use the principal susceptibilities of the C_2H_3 group as found from the extrapolation of the polyethylene anisotropy to 980% elongation.

$$K_{\parallel} = \chi_{\parallel} = K_3(C_2H_3) + K_3(C_6H_5) = -22.0 - 88.3 = -110.3$$
$$K_{\perp} = \chi_{\perp} = K_1(C_2H_3) + K_1(C_6H_5) = -20.2 - 34.4 = -54.6$$

Hence the maximum possible anisotropy for stretched polystyrene is

$$\chi_{\parallel} - \chi_{\perp} = -110.3 + 54.6 = -55.7 \text{ per repeating unit}$$

The last case is the poly-2,5-dichlorostyrene. As this polymer was stretched about 500%, we shall use the anisotropy of 520% elongated polyethylene in our calculation, but the change thus introduced is very small.

$$K = \chi_{\parallel} = K_3(C_2H_3) + K_3(C_6H_3Cl_2) = -21.5 - 118.3 = -139.8$$
$$K_{\perp} = \chi_{\perp} = K_1(C_2H_3) + K_1(C_6H_3Cl_2) = -20.4 - 64.4 = -84.8$$

Whence the maximum possible anisotropy for stretched poly-2,5-dichlorostyrene is

$$\chi_{\parallel} - \chi_{\perp} = -139.8 + 84.8 = -55.0$$

The maximum calculated anisotropies are about the same for the three polymer samples, as would be expected because the major contribution to the anisotropy of each sample has been attributed to the molecular anisotropy of the aromatic groups in each polymer.

Table III gives the maximum calculated anisotropy, the observed anisotropy and the percentage of the maximum which is actually developed. Some of the conclusions reached are summarized in Fig. 1.

TABLE III

COMPARISON OF CALCULATED AND OBSERVED ANISOTROPIES ($\times 10^6$)

Sample	Maximum Calcd.	Obsd.	Percentage
Polystyrene unoriented	−54.4	−0.8	1.5
Polystyrene stretched 980%	−55.7	−5.3	9.5
Poly-2,5-dichlorostyrene stretched ~500%	−55.0	−22.3	40.5

The magnetic effect of sequences of head-to-head or head-to-tail structure in a polystyrene chain is believed to be negligible for the single chain. However a polymer which was mainly of one structure or the other would probably become more

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[10] M. Ramanadhan, *Indian J. Phys.*, **4**, 15 (1929); K. Lonsdale, *Proc. Roy. Soc. (London)*, **171**, 541 (1939).

nearly crystalline when drawn than a polymer which was a random mixture of both structures and because of this greater degree of orientation would have an anisotropy closer to the maximum possible value.

It is clear that in unstretched polystyrene there is, as expected, a negligible preferred orientation of the aromatic groups, and that this preferred orientation remains small in stretched polystyrene. But the introduction of additional groups into the aromatic ring may cause a large preferred orientation. This conclusion is in agreement with the X-ray results reported by Baker.[11] The magnetic method described has obvious applications to other substituted polystyrenes and to related polymers.

Some confirmation of the calculations is to be found in the reported average susceptibility of −102 per repeating unit of poly-2,5-dichlorostyrene. This agrees reasonably well with the value of −101.0 calculated from Pascal's constants, and also with the value of $(2\,K_{\perp} + K_{\parallel})/3 = -103$ obtained from the maximum possible calculated principal susceptibilities.

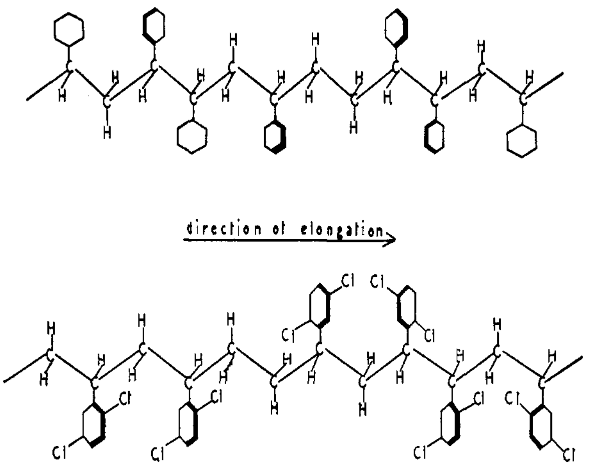

Fig. 1.—In oriented polystyrene the aromatic groups deviate only slightly from random orientation. In oriented poly-2,5-dichlorostyrene the aromatic groups assume a definite preferred direction such that the normals to the planes of the rings tend to be parallel to the direction of elongation.

EVANSTON, ILL.

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[11] W. O. Baker, in "High Polymers," edited by S. B. Twiss, Reinhold Publ. Corp., New York, N. Y., 1945, p. 141.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA S. A.]

Structural Studies on Polynuclear Pyridine Compounds

BY P. KRUMHOLZ

The ultraviolet absorption spectra and the basic dissociation constants of isomeric phenylpyridines, dipyridyls and phenanthrolines have been determined. Some correlations between the absorption spectra and the structure of the compounds have been discussed.

The study of the ultraviolet spectra of substituted biphenyls has provided valuable information on the structure of those compounds. It has been shown that the spectral properties are intimately connected with the electronic interaction between both benzene rings and that inhibition of this interaction by steric hindrance destroys the specific spectral behavior of the biphenyls.[1]

As benzene and pyridine show a similar spectroscopic behavior[2] it seemed to us to be of some interest to study the spectra of the isomeric phenylpyridines and dipyridyls and their salts, inasmuch as in this case relations between physical properties and molecular structure may be studied on sets of isomeric compounds.

We report below the ultraviolet absorption spectra of the three isomeric phenylpyridines, of the six isomeric dipyridyls, and of three isomeric phenanthrolines (ortho, meta and para), in the form of free bases, as well as of the corresponding mono- and bivalent pyridinium ions, and of the quaternary N-methylpyridinium ions. We present furthermore the data on the dissociation constants of the bases.

Experimental Part

Preparation and Purification of the Material.—The three isomeric phenylpyridines were prepared from benzene diazonium chloride and pyridine[3] separating the isomers by fractional crystallization of the picrates. The free bases were isolated by treating the picrates with an excess of 10% potassium hydroxide, filtering the potassium picrate and extracting the filtrate and the solid residue with ether. After drying with solid potassium hydroxide and evaporating the ether, the residue was distilled at 10^{-2} mm.

The dipyridyls were prepared from the product of the thermal decomposition of pyridine by fractional crystallization of the picrates as previously described.[4] The free bases were isolated in the same way as the phenylpyridines and purified by distillation and, whenever possible, by crystallization. γ,γ'-Dipyridyl was furthermore prepared by the action of metallic sodium on pyridine,[5] the α, β and β,β'-isomer by oxidation of meta and para phenanthroline with permanganate and subsequent decarboxylation of the dicarboxylic acids.[6]

Absorption spectra and dissociation constants of the compounds prepared by different methods were identical within experimental error. The three phenanthrolines were prepared by the commonly used Skraup synthesis from the corresponding phenylenediamines.

Melting points of the free bases and their picrates were identical with the data in the literature and are thus not

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[1] L. W. Pickett, G. F. Walter and H. France, THIS JOURNAL, **58**, 2296 (1936); M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940); B. Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

[2] See for instance H. Sponer, *J. Chem. Phys.*, **14**, 101 (1946).

[3] J. W. Haworth, I. H. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

[4] P. Krumholz, *Selecta Chimica*, **8**, 1 (1949).

[5] Anderson, *Ann.*, **154**, 274 (1870); C. R. Smith, THIS JOURNAL, **46**, 414 (1924).

[6] C. R. Smith, *ibid.*, **52**, 397 (1930).