

# Physical studies of nematic azoxybenzenes. II. Refractive indices and the internal field

W. H. de Jeu

Philips Research Laboratories, Eindhoven, The Netherlands

P. Bordewijk

Gorlaeus Laboratories of the University, Department of Physical Chemistry, Leiden, The Netherlands

(Received 17 June 1977)

The ordinary refractive index and the birefringence are reported for two homologous series of nematic liquid crystals, the *p,p'*-di-*n*-alkyl and *p,p'*-di-*n*-alkoxy azoxybenzenes. It is found that the high-frequency dielectric anisotropy is proportional to the anisotropy of the magnetic susceptibility. For axially symmetric molecules this proportionality allows a simplification of the intricate problem of the internal field, which can be taken as independent of the anisotropy of the surroundings of a molecule. Representing a molecule by a homogeneously polarizable spheroid, an equation is derived which relates the anisotropic high-frequency dielectric permittivity to the anisotropic molecular polarizability, and which gives consistent results for both the solid state and the nematic phase.

## I. INTRODUCTION

In the first paper of this series (hereafter referred to as part I) the anisotropic diamagnetic susceptibilities and the densities of a number of nematic liquid crystals were reported.<sup>1</sup> In this part we shall discuss results for the refractive indices of the same compounds. Like the magnetic susceptibility the refractive index is anisotropic, the ordinary refractive index  $n_0 \equiv n_{\perp}$  being smaller than the extraordinary one  $n_e \equiv n_{\parallel}$ . The subscripts  $\parallel$  and  $\perp$  refer to the directions parallel and perpendicular to the director, respectively. The birefringence of liquid crystals is one of their most spectacular properties, and measurements of the refractive indices are numerous.<sup>2-6</sup> However, the interpretation in terms of the electronic polarizability tensor of the molecules is complicated.

Let us consider the relation between the high-frequency permittivity tensor  $\epsilon$  (where  $\epsilon_{\gamma} = n_{\gamma}^2$ ,  $\gamma = \parallel, \perp$ ) and the electronic polarizability tensor of a molecule  $\alpha$ , which is a direct extension of the corresponding isotropic formula for the electric polarization  $P$  (Ref. 7):

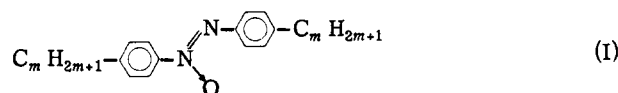
$$P = (\epsilon - I) \cdot E / 4\pi = N \langle \alpha \cdot E^i \rangle . \quad (1)$$

$I$  is the unit tensor,  $N$  is the particle density, while the brackets denote an average over the orientations of all molecules. Furthermore,  $E$  is the macroscopic field and  $E^i$  the internal field which is equal to the macroscopic field plus the field produced by the induced dipole moments of all other molecules. Hence the intricate problem of the internal field is here further complicated by the various anisotropies. Unlike the situation in molecular solids, where this combination of problems also occurs, in a nematic liquid the orientations of the molecules are not fixed, and the various quantities will in general depend on the order parameter  $S$ . If  $\theta$  is the angle between the long molecular axis and the director (axis of preferred orientation),  $S$  is defined as<sup>8</sup>

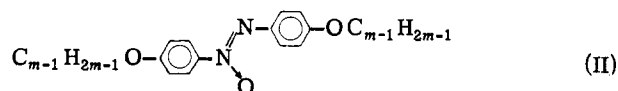
$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle . \quad (2)$$

The plan of the paper is as follows: Section II deals with the experimental methods used to determine  $n_{\perp}$  and

$\Delta n = n_{\parallel} - n_{\perp}$ . In Sec. III results for  $n_{\perp}$  and  $\Delta n$  at 546 and 633 nm are given for the series of *p,p'*-di-*n*-alkylazoxybenzenes



for  $m = 3-8$ , and for the series of *p,p'*-di-*n*-alkoxyazoxybenzenes



for  $m = 4-9$ . Using the results for the anisotropy of the magnetic susceptibility  $\Delta\chi$  from part I we find that as a function of temperature in the nematic phase  $\Delta\epsilon \equiv n_{\parallel}^2 - n_{\perp}^2 \sim \Delta\chi$ . If the molecules can be considered as effectively axially symmetric, then  $\Delta\chi \sim \rho S$  where  $\rho$  is the density (see part I), and we can conclude that  $\Delta\epsilon \sim \rho S$ . Taking this experimental fact into account a considerable simplification of the internal field problem results, which is discussed in Sec. IV. Representing a molecule by a homogeneously polarizable spheroid an approximate expression for the anisotropic internal field is derived. Section V gives a concluding discussion.

## II. EXPERIMENTAL

The refractive index in the isotropic phase of the compounds studied was measured with an Abbe refractometer (Zeiss model B), which gives a direct reading of  $n$  from the observation of a boundary line corresponding to the angle of total reflection. In the nematic phase  $n_{\perp}$  can be measured in a similar manner, contrary to  $n_{\parallel}$  which is usually larger than the refractive index of the standard glass prism. The intensity difference at the boundary line for the angle of total reflection corresponding to  $n_{\perp}$  can be increased by blocking the extraordinary light with a polarizer. The refractometer being calibrated for the yellow sodium line, the measured values  $n_R$  must be corrected in the case of other monochromatic light sources<sup>9</sup>:

$$n_{\perp} = n_R + F , \quad (3)$$

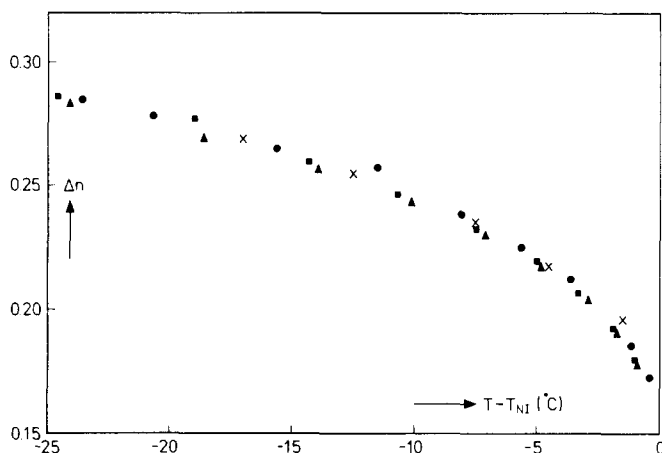


FIG. 1. Birefringence of PAA (series II,  $m=2$ ) at 633 nm; filled symbols are three independent measurements from this work, crosses are extrapolated values from Ref. 2(b).

with  $F = -0.0050$  for  $\lambda = 633$  nm (He-Ne-laser), and  $F = +0.0056$  for  $\lambda = 546$  nm (Hg-lamp with appropriate filters). The temperature was stabilized within  $0.1^\circ\text{C}$  by a circulating thermostated liquid.

In addition to  $n_{\perp}$  we directly measured  $\Delta n$  using an interference technique.<sup>10</sup> A uniform planar nematic layer is placed between crossed polarizers at  $45^\circ$  with the optical axis in a monochromatic light beam. The sample is put in a Mettler FP52 heating stage and heated or cooled at a rate of  $1^\circ/\text{min}$ , while the intensity of the transmitted light is recorded as a function of temperature. The intensity has a minimum value if

$$\Delta n d = k\lambda, \quad k = \text{integer}, \quad (4)$$

where  $d$  is the thickness of the cell. At the nematic-isotropic transition temperature,  $T_{\text{NI}}$ ,  $\Delta n$  changes discontinuously. Consequently the value of  $k$  for a certain minimum is not known yet. The value of  $k$  can be determined by placing the nematic sample at a fixed temperature (preferably near  $T_{\text{NI}}$ ) in a magnet with the variable magnetic field perpendicular to the layer. At sufficiently high fields the sample becomes homeotropic and  $k=0$ . Hence  $k$  is given by the number of minima in the transmitted light between the uniform planar situation at zero field and the homeotropic situation at high fields. As a check we used samples of different thickness. For  $d$  in Eq. (4) we used the spacing of the empty cell which was measured interferometrically.

### III. RESULTS

First the reproducibility of the measurements of  $\Delta n$  was investigated for the case of *p*-azoxyanisole (PAA, series II,  $m=2$ ). In Fig. 1 the results are given for  $\Delta n$  at 633 nm from three independent measurements and compared with literature values.<sup>2(b)</sup> The agreement is excellent. The absolute accuracy of  $\Delta n$  is about 1%, and that of  $n_{\perp}$  about  $\pm 0.0005$ . For both quantities the relative accuracy is much better. In Table I the results for  $n_{\perp}$  and  $\Delta n$  at 546 and 633 nm are given for the compounds of series I. The data are given as interpolated values

as a function of the temperature difference  $T - T_{\text{NI}}$ . Table II gives the results for the compounds of series II for  $m \geq 4$ . For  $m=2$  (PAA) and  $m=3$  (PAP, *p*-azoxyphenetole) extensive measurements at various wavelengths have been reported in the literature.<sup>2(a,b)</sup> In the case of series II the values for  $n_{\perp}$  at 546 nm are from Ref. 4(a).

As an illustration of the general behavior we consider the results for series I,  $m=5$ . Two trends are noteworthy. First we consider the average value  $\bar{\epsilon} = \frac{1}{3}(n_{\parallel}^2 + 2n_{\perp}^2)$ . In Eq. (1) the particle density is given by  $N = N_A \rho / M$ , where  $N_A$  is Avogadro's number and  $M$  the mass number. Hence the macroscopic quantity to be compared with polarizability and internal field is  $\bar{\epsilon} / \rho$ . In the nematic phase of compound (I,  $m=5$ )  $\bar{\epsilon}$  varies from 2.59 at room temperature to about 2.52 at  $T_{\text{NI}}$ , and in the isotropic phase from 2.506 at  $T_{\text{NI}}$  to 2.496 at  $75^\circ$ . However,  $\bar{\epsilon} / \rho$  is constant to a very good approximation, the deviations from the average value over the whole temperature range where measurements have been made being  $< 0.5\%$ . This continuous behavior of  $\bar{\epsilon} / \rho$  at the phase transition has also been found for the static dielectric permittivity of nonpolar liquid crystals.<sup>11</sup> Secondly we consider  $\Delta\epsilon = n_{\parallel}^2 - n_{\perp}^2$ , which varies roughly by a factor of two in the nematic phase of (I,  $m=5$ ). From part I we note that  $\Delta\chi^f$  varies by the same factor, and we find that  $\Delta\epsilon / \Delta\chi$  (where  $\Delta\chi = \rho \Delta\chi^f$ ) is approximately constant. The deviations from the average value of  $\Delta\epsilon / \Delta\chi$  are never more than 1% over the whole nematic temperature range. Assuming that the molecules are axially symmetric due to effectively free rotation around the long molecular axis,  $\Delta\chi^f$  is proportional to the order parameter  $S$  (see part I). Hence we find within the experimental accuracy

$$\Delta\epsilon \sim NS. \quad (5)$$

This proportionality is also found for the other compounds investigated (see Fig. 2). For all the compounds studied the deviation of  $\Delta\epsilon / \Delta\chi$  from the average value never exceeds 3%.

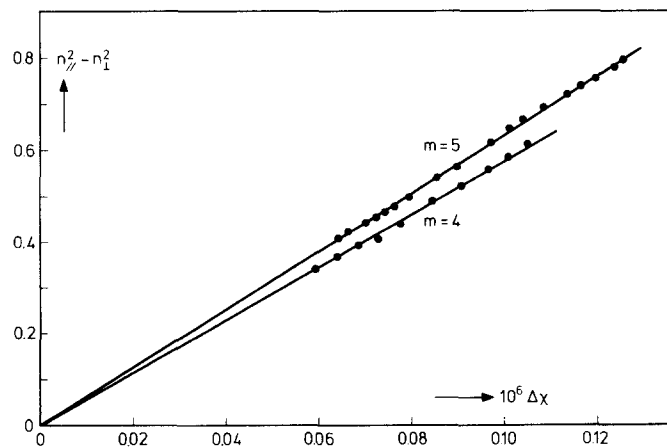


FIG. 2. Relation between  $n_{\parallel}^2 - n_{\perp}^2$  (at 546 nm) and the anisotropy of the volume susceptibility (cgs units) in the nematic phase of two compounds of series I.

TABLE I. Refractive indices of the compounds of series I.

$T - T_{NI}$	546 nm		633 nm		546 nm		633 nm		546 nm		633 nm	
	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$
	$m=3$				$m=4$				$m=5$			
10	1.5926	...	1.6081	...	1.5886	...	1.6062	...	1.5623	...	1.5784	...
5	42	...	1.6100	...	1.5908	...	88	...	48	...	1.5809	...
1	54	...	15	...	25	...	1.6108	...	68	...	29	...
-0.5	1.5520	0.1373	1.5641	0.1221	1.5600	0.1050	1.5734	0.0990	1.5290	0.1280	1.5419	0.1093
-1	00	484	21	325	1.5570	158	10	0.1084	75	363	1.5395	182
-2	1.5471	612	1.5591	448	35	278	1.5672	208	48	486	63	283
-3	50	716	65	538	13	367	50	289	30	581	43	390
-5	17	854	34	659	1.5486	498	24	413	09	718	21	502
-10	1.5379	0.2084	1.5486	871	54	708	1.5579	630	1.5182	922	1.5290	694
-15	58	277	61	0.2019	33	845	56	782	63	0.2061	69	823
-20	50	...	51	140	...	...	...	...	49	158	54	924
-30	...	...	...	...	...	...	...	...	44	313	41	0.2079
-40	...	...	...	...	...	...	...	...	49	433	44	197
	$m=6$				$m=7$				$m=8$			
10	1.5587	...	1.5744	...	...	...	...	...	...	...	...	...
5	1.5610	...	64	...	1.5459	...	1.5600	...	1.5419	...	1.5552	...
1	28	...	81	...	82	...	22	...	30	...	67	...
-0.5	1.5324	0.0953	1.5435	0.0853	1.5147	0.1223	1.5250	0.1018	1.5088	0.1204	1.5194	0.0996
-1	1.5296	0.1062	14	975	21	307	23	113	61	320	62	0.1097
-2	67	185	1.5382	0.1107	1.5097	434	1.5196	220	24	478	15	256
-3	46	274	62	187	81	514	79	297	1.4935 <sup>b</sup>	...	1.5012 <sup>b</sup>	...
-5	19	405	31	300	54	642	51	408	28 <sup>b</sup>	...	05 <sup>b</sup>	...
-10	1.5184	608	1.5281	488	20	835	10	591	24 <sup>b</sup>	...	05 <sup>b</sup>	...
-15	67	743	62	612	1.4999	954	1.5087	726	32 <sup>b</sup>	...	12 <sup>b</sup>	...
-20	56	846	54	714	75 <sup>a</sup>	...	57 <sup>a</sup>	...	43 <sup>b</sup>	...	22 <sup>b</sup>	...
-30	46	0.2004	46	871	84 <sup>a</sup>	...	65 <sup>a</sup>	...	62 <sup>b</sup>	...	43 <sup>b</sup>	...
-40	...	...	...	...	1.5002 <sup>a</sup>	...	90 <sup>a</sup>	...	...	...	...	...

<sup>a</sup>In smectic A phase,  $S_{AN}$  transition at  $T - T_{NI} = 16.7^\circ\text{C}$ .<sup>b</sup>In smectic A phase,  $S_{AN}$  transition at  $T - T_{NI} = 2.2^\circ\text{C}$ .TABLE II. Refractive indices of the compounds of series II [values for  $n, n_1$  at 546 nm from Ref. 4(a)].

$T - T_{NI}$	546 nm		633 nm		546 nm		633 nm		546 nm		633 nm	
	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$	$n, n_1$	$\Delta n$
	$m=4$				$m=5$				$m=6$			
10	1.604	...	...	...	1.581	...	...	...	1.573	...	1.5560	...
5	...	...	1.5850	...	...	...	1.5737	...	...	...	75	...
1	1.609	...	69	...	1.584	...	62	...	1.578	...	90	...
-0.5	...	0.1562	1.5343	0.1408	...	0.1484	1.5167	0.1353	...	0.1395	1.5132	0.1060
-1	1.550	680	23	493	1.532	583	52	451	1.531	500	16	158
-2	...	833	1.5285	607	...	726	21	558	...	638	1.5092	284
-3	...	939	69	686	...	820	1.5095	645	...	736	76	368
-5	1.539	0.2104	41	807	1.520	979	63	776	1.520	884	59	488
-10	4	383	04	0.2022	1.516	0.2232	24	992	1.515	0.2118	29	683
-15	1	576	...	175	2	411	04	0.2147	1	275	05	826
-20	0	741	...	...	0	553	1.4985	271	0	398	1.4991	940
-30	...	...	...	...	1.508	802	74	479	1.509	600	79	0.2136
-40	...	...	...	...	...	...	...	...	8	...	81	292
	$m=7$				$m=8$				$m=9$			
10	1.558	...	...	...	1.553	...	...	...	1.543	...	...	...
5	...	...	1.5432	...	...	...	1.5379	...	...	...	1.5293	...
1	1.564	...	44	...	1.557	...	95	...	1.548	...	1.5307	...
-0.5	...	0.1340	1.5054	0.1218	...	0.1154	1.5002	0.1022	...	0.1241	1.4920	0.1058
-1	1.508	466	25	300	1.514	272	1.4984	108	1.505	324	1.4897	162
-2	...	625	1.4998	416	...	434	64	210	...	464	72	285
-3	...	717	82	502	...	540	45	287	...	539	57	363
-5	1.503	864	56	623	1.504	691	16	400	1.495	677	37	483
-10	0	0.2100	14	822	1.499	928	1.4877	593	1.489	892	1.4796	674
-15	1.497	258	1.4892	956	5	0.2088	58	733	7	0.2010	61	807
-20	5	384	78	0.2062	4	216	45	841	...	...	...	...
-30	4	576	68	226	2	383 <sup>a</sup>	36 <sup>a</sup>	0.2186 <sup>a</sup>	...	...	...	...
-40	4	723	77	354	...	...	...	...	...	...	...	...

<sup>a</sup>At  $T - T_{NI} = 28^\circ\text{C}$ .

#### IV. THEORY OF THE INTERNAL FIELD

Basic to our discussion of the internal field in nematics is the observation that, within the accuracy of the measurements, the high-frequency dielectric anisotropy  $\Delta\epsilon$  is proportional to the product  $NS$  [Eq. (5)]. While such a proportionality is obvious in the case of the diamagnetic susceptibility, where the field working on a molecule can be taken equal to the macroscopic field, it is somewhat surprising in the case of the dielectric permittivity. Since the internal field should be a linear function of the macroscopic field, its relation to the macroscopic field can be represented by:

$$\mathbf{E}^i = \mathbf{K} \cdot \mathbf{E} \quad (6)$$

where  $\mathbf{K}$  is a normal second-rank tensor that one expects to depend both on the properties and the orientation of the molecule at which the internal field is considered and on the dielectric tensor  $\epsilon$  of the macroscopic sample.<sup>12</sup> With Eq. (6) the induced polarization [see Eq. (1)] becomes:

$$\mathbf{P} = N \langle \alpha \cdot \mathbf{K} \rangle \cdot \mathbf{E} \quad (7)$$

This yields for the dielectric permittivity tensor:

$$\epsilon = \mathbf{1} + 4\pi N \langle \alpha \cdot \mathbf{K} \rangle \quad (8)$$

Consequently we find for the dielectric anisotropy

$$\Delta\epsilon = 4\pi N (\langle \alpha \cdot \mathbf{K} \rangle_{\parallel} - \langle \alpha \cdot \mathbf{K} \rangle_{\perp}) \quad (9)$$

It follows that  $\mathbf{K}$  should behave in such a way that the statistical average at the right-hand side of Eq. (9) is proportional to the order parameter  $S$ . As the molecules are assumed to be effectively axially symmetric we have at the other hand

$$S = (\langle \alpha \rangle_{\parallel} - \langle \alpha \rangle_{\perp}) / (\alpha_{\parallel} - \alpha_{\perp}) \quad (10)$$

where  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the principal values of the polarizability tensor,  $\alpha_{\parallel}$  being along the long molecular axis.

We did not succeed in deriving an expression for  $\mathbf{K}$  from a molecular model that yields the observed proportionality. A sufficient condition for it is that the tensor  $\mathbf{K}$  for a molecule with given orientation is independent of the dielectric anisotropy of the macroscopic sample, and thus independent of the orientation of the molecule with respect to the director. It then follows that the principal axes of  $\alpha$  and  $\mathbf{K}$  should coincide. Then the average at the right-hand side of Eq. (8) can be expressed in molecular properties and the order parameter [Eq. (2)], yielding

$$\begin{aligned} \epsilon_{\parallel} &= 1 + \frac{4}{3} \pi N [\alpha_{\parallel} K_{\parallel} (2S + 1) + \alpha_{\perp} K_{\perp} (2 - 2S)] \quad (11) \\ \epsilon_{\perp} &= 1 + \frac{4}{3} \pi N [\alpha_{\parallel} K_{\parallel} (1 - S) + \alpha_{\perp} K_{\perp} (2 + S)] \end{aligned}$$

where  $K_{\parallel}$  and  $K_{\perp}$  are the principal values of  $\mathbf{K}$ .

To obtain in Eq. (11) reasonable values for  $K_{\parallel}$  and  $K_{\perp}$ , we consider the case of ideal ordering,  $S=1$ . For that case the values of  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  will be approximately equal to those for the solid, if in the solid all molecules have the same orientation. Vuks<sup>13</sup> suggested that the internal field in a solid with less than cubic symmetry is independent of the orientation, and is given by:

$$\mathbf{E}^i = \frac{1}{3} (\bar{\epsilon} + 2) \mathbf{E} \quad (12)$$

For systems with cubic symmetry this reduces to Lorentz' expression for the internal field which is known to be an exact result for that case.<sup>14</sup> Equation (12) makes the tensor  $\mathbf{K}$  isotropic. Substituting this result into Eq. (11) one obtains the formula by Maier and Meier for nonpolar liquid crystals.<sup>15</sup>

There are a number of objections to Eq. (12), however. In the first place this equation lacks a molecular basis even for the case of solids, which is much simpler than the case of liquid crystals. The agreement obtained by Vuks between the optical anisotropies determined from the refractive index in the crystal and from light scattering in solution should be treated with caution, since the light scattering experiment yields apparent anisotropies which, in view of the anisotropy of the molecular shape, one would expect to be smaller than the real anisotropies. This is easily seen if one realizes that immersion of a macroscopic ellipsoid with isotropic refractive index in a liquid having the same refractive index does not introduce any optical anisotropy, although the polarizability of the ellipsoid is anisotropic.

In a number of cases Vuks' treatment yields rather implausible results. For PAA and PAP the refractive indices in the solid state have been reported.<sup>16</sup> All three principal refractive indices of the crystal show normal dispersion, which is much larger for the principal axis close to the long axis of the molecules than for the other two axes. Consequently in these systems the polarizability components perpendicular to the long axis of the molecule show anomalous dispersion when calculated with Eq. (12). Furthermore, in iodoform the refractive index along the three-fold axis of the molecules is larger than the refractive index perpendicular to that axis,<sup>17</sup> yielding with Vuks' equation a positive anisotropy of the polarizability, whereas measurements of the Kerr effect show that the anisotropy is negative.<sup>18</sup>

Instead of Eq. (12) it seems preferable to write the internal field in a solid crystal as:

$$\mathbf{E}^i = \mathbf{E} + 4\pi \mathbf{L} \cdot \mathbf{P} \quad (13)$$

where  $\mathbf{L}$  is the Lorentz tensor.<sup>17,19-21</sup> Equation (13) is an exact result for systems of identical point polarizabilities with parallel principal axes that are also positionally equivalent. The principal values of  $\mathbf{L}$  can then be calculated from the lattice structure. The form of Eq. (13) used by Neugebauer<sup>19</sup> has been particularly popular in the applications to liquid crystals.<sup>5,8,22</sup> The assumption of point polarizabilities may introduce considerable errors, however, if the polarizability of a molecule is distributed anisotropically in space. For this reason it seems preferable to consider both a molecule and its surroundings on a continuum basis, and to approximate a molecule by an anisotropic homogeneously polarizable spheroid, filling up the cavity in the anisotropic homogeneously polarized continuum. This model yields the same expression for  $\mathbf{E}^i$  as given in Eq. (13), where the principal values of  $\mathbf{L}$  are now equal to the depolarizing factors  $\Omega_{\parallel}$  and  $\Omega_{\perp}$  occurring in the solution of the electrostatic problem of a dielectric spheroid in an

TABLE III. Estimated values for  $a$  and  $b$  in the internal field calculation, and resulting values for the electronic polarizabilities (in  $\text{\AA}^3$ ) for series I.

$m$	546 nm			633 nm				
	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$
3	19.5	6.67	69	28	41	66	28	38
4	21.7	6.60	76	32	45	74	31	43
5	24.3	6.70	86	34	52	81	34	47
6	26.8	6.65	91	37	54	87	37	50
7	29.2	6.69	101	40	61	94	40	54
8	31.7	6.67	104	44	60	97	44	54

external electric field.<sup>23</sup> For a prolate spheroid these factors are:

$$\Omega_i = 1 - w^2 + \frac{1}{2}w(w^2 - 1) \ln[(w+1)/(w-1)] , \quad (14)$$

$$\Omega_t = \frac{1}{2}(1 - A_i) ,$$

with  $w^2 = a^2/(a^2 - b^2)$ , if  $a$  and  $b$  are the long and short axes of the spheroid. Equation (13) is then equivalent to taking the polarizability of the molecule equal to that of a homogeneously polarizable spheroid with the size of the molecule and dielectric permittivity tensor equal to that of the macroscopic sample.<sup>24</sup> Substituting Eq. (7) for  $P$  in Eq. (13) it follows that in this case the principal values of the tensor  $\mathbf{K}$  are given by

$$K_i = (1 - 4\pi N\alpha_i \Omega_i)^{-1} , \quad (15)$$

$$K_t = (1 - 4\pi N\alpha_t \Omega_t)^{-1} .$$

Apart from a slight variation due to the density dependence, this equation fulfills the requirement that the internal field should depend only on the angle between the molecule and the macroscopic field, and does not depend on the macroscopic dielectric anisotropy.

With Eq. (15), Eq. (11) yields:

$$\epsilon_{\parallel} = 1 + \frac{4}{3}\pi N \left[ \frac{\alpha_i(2S+1)}{1 - 4\pi N\alpha_i \Omega_i} + \frac{\alpha_t(2-2S)}{1 - 4\pi N\alpha_t \Omega_t} \right] , \quad (16)$$

$$\epsilon_{\perp} = 1 + \frac{4}{3}\pi N \left[ \frac{\alpha_i(1-S)}{1 - 4\pi N\alpha_i \Omega_i} + \frac{\alpha_t(2+S)}{1 - 4\pi N\alpha_t \Omega_t} \right] .$$

These expressions make it possible to infer  $\alpha_i$  and  $\alpha_t$  from the experimental values of  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$ , if the density and the order parameter are known, with

$$\alpha_i = \frac{1}{4\pi N} \left[ \Omega_i + \frac{1}{\epsilon_{\perp} - 1 + \frac{1}{3}(\epsilon_{\parallel} - \epsilon_{\perp})(1+2/S)} \right]^{-1} , \quad (17)$$

$$\alpha_t = \frac{1}{4\pi N} \left[ \Omega_t + \frac{1}{\epsilon_{\perp} - 1 + \frac{1}{3}(\epsilon_{\parallel} - \epsilon_{\perp})(1-1/S)} \right]^{-1} .$$

The values obtained depend on the value of the ratio  $a/b$  used. Results for the compounds of series I and II will be discussed in the next section.

### The isotropic liquid

Equation (16) makes  $\bar{\epsilon}$  equal to the value of  $\epsilon$  for the isotropic liquid, i. e., for  $S=0$ :

$$\epsilon = 1 + \frac{4}{3}\pi N \left[ \frac{\alpha_i}{1 - 4\pi N\alpha_i \Omega_i} + \frac{2\alpha_t}{1 - 4\pi N\alpha_t \Omega_t} \right] . \quad (18)$$

This is in agreement with the experimental results. Equation (18) deviates from the Clausius-Mossotti equation, however, which is equivalent to:

$$\epsilon = 1 + \frac{4\pi N\bar{\alpha}}{1 - \frac{4}{3}\pi N\bar{\alpha}} . \quad (19)$$

For the compounds investigated, both  $\alpha_i \Omega_i$  and  $\alpha_t \Omega_t$  are smaller than  $\bar{\alpha}/3$ , so that Eq. (18) yields smaller values of  $\epsilon$  than Eq. (19). A direct test of these equations needs values of  $\alpha_i$  and  $\alpha_t$  determined independently by a method in which the problem of the internal field is avoided. This is only possible in the gaseous state, but in this state a sufficient concentration of the large molecules of compounds that form liquid crystals cannot be obtained at temperatures that are low enough to prevent decomposition.

A strongly anisotropic molecule for which values of  $\alpha_i$  and  $\alpha_t$  are known from measurements in the gaseous state, but that does not form a nematic phase, is carbon disulphide. From the average polarizability in the optical frequency range<sup>25</sup> one obtains with the Lorenz-Lorentz equation  $n=1.652$  at  $20^\circ\text{C}$ . The experimental result is  $n_D^{20}=1.6255$ , however. Clearly, for carbon disulphide the value calculated with the Lorenz-Lorentz equation is too high. To apply Eq. (18) we use the value of  $\alpha_i - \alpha_t$  determined by Boogaard *et al.*<sup>26</sup> from the temperature dependence of the Kerr effect in the gas. With  $a/b=2.0$  one then obtains with Eq. (18) at  $20^\circ\text{C}$   $n=1.611$ , which is closer to the experimental value than the Lorenz-Lorentz value. It follows that the deviation from the Clausius-Mossotti equation implied by Eq. (18) may be not unrealistic.

## V. DISCUSSION

In order to calculate  $\alpha_i$  and  $\alpha_t$  for a particular compound with Eq. (17), we have to estimate a value for the ratio  $a/b$ . For the present series we adopt the following procedure:  $a$  is taken equal to the length of the all-stretched molecule, which is calculated from molecular models. Using the densities from part I,  $b$  is chosen such that the volume of the spheroid is equal to the volume available to a molecule in the nematic phase at  $T_{NI}$ . The results for the compounds of series I and II are given in Tables III and IV, respectively. For PAA and PAP we used literature values for the refractive indices,

TABLE IV. Estimated values for  $a$  and  $b$  in the internal field calculation, and resulting values for the electronic polarizabilities (in  $\text{\AA}^3$ ) for series II.

$m$	546 nm			633 nm				
	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$
2	17.4	6.40	67	22	44	61	22	39
3	19.9	6.54	77	25	52	72	25	47
4	22.2	6.52	81	29	52	75	29	46
5	24.6	6.57	90	31	59	85	32	53
6	27.2	6.54	98	35	63	88	35	53
7	29.7	6.57	106	37	68	99	38	61
8	32.3	6.56	111	41	70	103	41	62
9	34.7	6.57	119	43	76	112	43	69

taken from Ref. 2(b). From Tables III and IV we note that the value of  $\alpha_i - \alpha_t$  increases with increasing chain length  $m$ . On this trend an alternation is superimposed in the sense that the increase in  $\alpha_i - \alpha_t$  from  $m$  to  $m+1$  is relatively small (or even negative) if  $m$  is odd, and relatively large when  $m$  is even. This alternation parallels the well-known alternation of  $T_{NI}$ . In Maier and Saupe's molecular-statistical theory of the nematic phase<sup>27</sup> the orientational order is attributed to the anisotropic part of the dispersion forces (London-van der Waals forces). Then one can derive that approximately

$$T_{NI} \sim (\alpha_i - \alpha_t)^2 / V^2 \quad (20)$$

Although the anisotropic polarizability is not necessarily the dominant factor in determining nematic behavior, this proportionality has been shown to be qualitatively correct for the present series.<sup>28</sup>

For PAA and PAP we can use Eq. (17) with  $S=1$  to determine  $\alpha_i$  and  $\alpha_t$  from the refractive indices in the solid state.<sup>16</sup> The results are given for various wavelengths in Tables V and VI. First  $\alpha_i$  and  $\alpha_t$  were calculated with the  $a/b$  value also used for the nematic phase. Slightly different values for  $a$  and  $b$  can be generated from the crystallographic data.<sup>16,29,30</sup> This second set of values is obtained with  $a$  as the cross section of the unit cell along the optical axis, and  $b$  chosen such that the volume of the spheroid is equal to the volume available to a molecule in the solid state. For PAA the values for  $\alpha_i$ , and thus also for  $\alpha_i - \alpha_t$ , are somewhat smaller with the latter choice of  $a/b$ ; for PAP the differences are of minor significance. For  $\lambda = 546$  nm the results can be compared with those obtained in the nematic phase. For PAA the agreement is good, only  $\alpha_i$  differs a few percent; for PAP the solid state value of  $\alpha_i$  is about 10% larger than that from the nematic phase. Taking account of the uncertainties in the appropriate shape factors of the two phases, in the density of the solid, and in the choice of the long molecular axis, which in the solid is not necessarily along the direction of highest refractivity, we conclude that the overall agreement is satisfactory.

For comparison Tables V and VI also give results for  $\alpha_i$  and  $\alpha_t$  of PAA and PAP, calculated from Eq. (11) with  $S=1$  and  $K_i = K_t$  according to Eq. (12) (Vuks' formula). Note the anomalous dispersion of  $\alpha_t$ , which is not present in the previously discussed results. For PAA the values of  $\alpha_i$ ,  $\alpha_t$ , and  $\alpha_i - \alpha_t$  from Vuks' formula are somewhat smaller than the earlier results. This difference is already larger for PAP, and increases with increasing  $a/b$  ratio. Nevertheless the order of

TABLE V. Electronic polarizabilities (in  $\text{\AA}^3$ ) of PAA as obtained from the refractive indices in the solid state (see text).

		$a=17.4 \text{ \AA}, b=6.40 \text{ \AA}$		$a=14.9 \text{ \AA}, b=6.36 \text{ \AA}$				Eq. (12)		
$\lambda$	(nm)	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$
546	69.3	22.5	46.8	65.1	22.7	42.4	58.3	20.7	37.6	
589	66.1	22.3	43.8	62.3	22.5	39.8	55.4	20.8	34.6	
650	62.8	22.1	40.7	59.4	22.4	37.0	52.5	21.0	31.5	

TABLE VI. Electronic polarizabilities (in  $\text{\AA}^3$ ) of PAP as obtained from the refractive indices in the solid state (see text).

		$a=19.9 \text{ \AA}, b=6.54 \text{ \AA}$		$a=15.9 \text{ \AA}, b=6.24 \text{ \AA}$				Eq. (12)		
$\lambda$	(nm)	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$	$\alpha_i$	$\alpha_t$	$\alpha_i - \alpha_t$
492	85.0	26.3	58.7	84.3	26.3	57.9	68.8	24.4	44.4	
546	77.4	26.0	51.4	76.8	26.0	50.8	62.5	24.7	37.8	
589	74.3	25.8	48.5	73.7	25.9	47.9	59.5	24.9	34.6	
650	70.4	25.5	44.9	69.9	25.6	44.3	56.8	24.9	31.9	

magnitude of the results is still correct in these cases. Comparing Eq. (12) and Eq. (15) we note that both expressions are equivalent when

$$\Omega_\gamma = \frac{1}{3}(\bar{\epsilon} - 1)/(\epsilon_\gamma - 1), \quad \gamma = \parallel, \perp \quad (21)$$

For the present compounds the largest value of  $\epsilon_\gamma$  corresponds to the longest axis of the molecule for which  $\Omega_\gamma < \frac{1}{3}$ , and Eq. (21) is approximately valid. If the largest value of  $\epsilon_\gamma$  corresponds to a short axis of the molecule, however, Vuks' formula might even give an incorrect sign of the anisotropy of the polarizability (as discussed in the previous section for iodoform).

Recently Barbero *et al.*<sup>31</sup> also discussed the optical properties of nematic liquid crystals, using a formalism that does not depend on the proportionality given in Eq. (5). However, using data from Refs. 2(c) and 32 we found that Eq. (5) is also valid for the case of *N*-(*p*-methoxybenzylidene)-*p'*-*n*-butylaniline, MBBA, which they discuss. Therefore we feel that their formalism is unnecessarily complicated compared with Vuks' and our treatment, which are both compatible with Eq. (5). Furthermore it should be noted that in Ref. 31 Vuks' formula is incorrectly stated with  $\bar{\epsilon} = (n_{\parallel}^2 + n_{\perp}^2)/2$  instead of  $\bar{\epsilon} = (n_{\parallel}^2 + 2n_{\perp}^2)/3$ . Hence no conclusions can be drawn from the comparison of the two formalisms in Ref. 31.

In conclusion we have derived an equation that relates the anisotropic high-frequency dielectric permittivity to the anisotropic molecular polarizability, assuming that a molecule can be represented by an anisotropic but homogeneously polarizable spheroid. The internal field is taken independent of the dielectric anisotropy, which makes the formula not only applicable to molecular solids, but also to nematic liquid crystals. In the latter case the form of the internal field is motivated by the experimental observation that  $\Delta\epsilon \sim NS$ .

In the subsequent paper the application of the above formalism for the internal field to the Kirkwood-Fröhlich equation for the permittivity of polar nematics will be discussed.

## ACKNOWLEDGMENT

The authors wish to thank W. A. P. Claassen for his technical assistance.

<sup>1</sup>W. H. de Jeu and W. A. P. Claassen, *J. Chem. Phys.* **68**, 102 (1978), preceding paper.

<sup>2</sup>(a) O. Pellet and P. Chatelain, *Bull. Soc. Min. Crystallogr.* **73**, 154 (1950); (b) P. Chatelain and M. Germain, *C. R.*

- Acad. Sci. **259**, 127 (1964); (c) M. Brunet-Germain, *ibid.* B **271**, 1075 (1970).
- <sup>3</sup>(a) G. Pelzl and H. Sackmann, Symp. Faraday Soc. **5**, 68 (1971); (b) H. Schulze and W. Burkersrode, Exp. Tech. Phys. **23**, 369 (1975); (c) G. Pelzl, R. Rettig, and D. Demus, Z. Phys. Chem. (Leipzig) **256**, 305 (1975).
- <sup>4</sup>(a) V. N. Tsvetkov, E. I. Ryumtsev, I. P. Kolomiets, A. P. Kovshik, and N. L. Gantseva, Opt. Spectrosk. **35**, 511 (1973); (b) A. P. Kovshik, Yu. I. Denite and E. I. Ryumtsev, Sov. Phys. Crystallogr. **20**, 532 (1976).
- <sup>5</sup>I. Haller, H. A. Huggins, H. R. Lilienthal, and T. R. McGuire, J. Phys. Chem. **77**, 950 (1973).
- <sup>6</sup>E. G. Hanson and Y. R. Shen, Mol. Cryst. Liq. Cryst. **36**, 193 (1976).
- <sup>7</sup>C. J. F. Böttcher, *Theory of Electric Polarization*, 2nd ed. (Elsevier, Amsterdam, 1973), Vol. I.
- <sup>8</sup>A. Saupe and W. Maier, Z. Naturforsch. **16a**, 816 (1961).
- <sup>9</sup>R. Rath, Neues Jb. Mineral. Abh. **90**, 1 (1957).
- <sup>10</sup>(a) D. A. Balzarini, Phys. Rev. Lett. **25**, 914 (1970); (b) W. H. de Jeu, Solid State Commun. **13**, 1521 (1973).
- <sup>11</sup>W. H. de Jeu and Th. W. Lathouwers, Z. Naturforsch. **29a**, 905 (1974).
- <sup>12</sup>A. N. Kuznetsov, V. A. Livshits, and S. G. Cheskis, Sov. Phys. Crystallogr. **20**, 142 (1975).
- <sup>13</sup>M. F. Vuks, Opt. Spectrosk. **20**, 361 (1966).
- <sup>14</sup>Reference 7, p. 167.
- <sup>15</sup>W. Maier and G. Meier, Z. Naturforsch. **16a**, 262 (1961).
- <sup>16</sup>P. Chatelain, C. R. Acad. Sci. **203**, 266 and 1169 (1936).
- <sup>17</sup>D. A. Dunmur, Mol. Phys. **23**, 109 (1972).
- <sup>18</sup>R. J. W. le Fèvre and G. L. D. Ritchie, J. Chem. Soc. **1963**, 4933.
- <sup>19</sup>H. E. J. Neugebauer, Can. J. Phys. **32**, 1 (1954).
- <sup>20</sup>A. P. Minton, J. Phys. Chem. **76**, 886 (1972).
- <sup>21</sup>J. H. P. Colpa, Physica **56**, 185 and 205 (1971).
- <sup>22</sup>(a) H. S. Subramanyam and D. Krishnamurti, Mol. Cryst. Liq. Cryst. **22**, 239 (1973); (b) H. S. Subramanyam, C. S. Prabha, and D. Krishnamurti, *ibid.* **28**, 201 (1974).
- <sup>23</sup>Reference 7, pp. 79, 141.
- <sup>24</sup>P. Bordewijk, Physica **75**, 146 (1974).
- <sup>25</sup>H. A. Stuart, *Molekülstruktur*, 3e Auflage (Springer, Berlin, 1967), p. 416.
- <sup>26</sup>M. P. Boogaard, A. D. Buckingham, and G. L. D. Ritchie, Mol. Phys. **18**, 575 (1970).
- <sup>27</sup>W. Maier and A. Saupe, Z. Naturforsch. **14a**, 882 (1959); **15a**, 287 (1960).
- <sup>28</sup>W. H. de Jeu and J. van der Veen, Mol. Cryst. Liq. Cryst. **40**, 1 (1977).
- <sup>29</sup>(a) W. R. Krigbaum, Y. Chatani, and P. G. Barber, Acta Cryst. Sect. B **26**, 97 (1970); (b) C. H. Carlisle and C. H. Smith, *ibid.* **27**, 1068 (1971).
- <sup>30</sup>J. D. Bernal and D. Crowfoot, Disc. Faraday Soc. **29**, 1032 (1933).
- <sup>31</sup>D. Barbero, R. Malvano, and M. Omini, Mol Cryst. Liq. Cryst. **39**, 69 (1977).
- <sup>32</sup>W. H. de Jeu, W. A. P. Claassen, and A. M. J. Spruijt, Mol. Cryst. Liq. Cryst. **37**, 269 (1976).

**Erratum: Physical studies of nematic azoxybenzenes. II.  
Refractive indices and the internal field  
[J. Chem. Phys. 68, 109 (1978)]**

W. H. de Jeu

*Philips Research Laboratories, Eindhoven, Netherlands*

P. Bordewijk

*Gorlaeus Laboratories of the University, Department of Physical Chemistry, Leiden, Netherlands*

In the above paper the values for the ordinary refractive index at 546 nm and 633 nm of the series of *p, p'*-dialkylazoxybenzenes, given in Table I, should be interchanged. Consequently, the dispersion of the refractive index is normal. The results for  $\Delta n$  have been placed correctly.

**Erratum: Effects of collisions on the magnetic quenching  
of positronium  
[J. Chem. Phys. 62, 2646 (1975)]**

Allen P. Mills, Jr.

*Bell Laboratories, Murray Hill, New Jersey 07974*

The following errors should be noted:

1. On p. 2649, the matrix for  $A_0$  should have a +1 entry in the sixth row, fifth column, instead of -1 as shown.

2. In Eq. (27), the  $-\frac{1}{4}$  factors should read  $+\frac{1}{4}$ ; the factor  $(ab - db - rs)$  should read  $(ab + db + 2rs)$ .

3. Immediately after Eq. 27, the term  $-\det A'$  should read  $+\det A'$ .

4. Two sentences later, the factor  $(1 - q^2)$  should read  $(1 + q^2)$ .

5. In Eq. 4, the time derivative has been omitted from the left-hand side.

These changes do not affect the explicit calculations in this paper.