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Halide Effect in L(+) Glutamic Acid Halogen Acid Salts

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L(+) glutamic acid halogen acid salts [$HOOC(CH_2)_2CH(NH_2)COOH \cdot HX$], with X = Cl, Br, I, and mixed crystals of the hydrochloride and hydrobromide were studied by crystallographic, optical, and calorimetric methods. All three salts are isostructural, crystallizing in the orthorhombic space group $P2_12_12_1$. The linear polarizability follows the general scheme I > Br > Cl but the specific refractive energy contributions of the halides to the refractive indices are less than predicted by factors of 12 and 2, respectively. The first nonlinear polarizability follows the trend Cl = Br > I and is ascribed to the electronic nature of the nonlinear optical polarizability of the hydrogen bonds. The anomalous behavior of the hydroiodide is attributed to the different molecular spatial arrangement.

Introduction

Large optically clear single crystals of L(+) glutamic acid hydrochloride [$HOOC(CH_2)_2CH(NH_2)COOH \cdot HCl$], a nonlinear optical material, were grown reproducibly from aqueous solutions (*1*). Type I phase matching for optical second harmonic generation at 1.06 μm was demonstrated with $d_{36} = 0.32 \pm 0.09\, d_{36}$ ADP (*1, 2*). The crystals are transparent from 235.5 nm to 1.71 μm (*1*) and the refractive indices as a function of wavelength were measured (*2*).

From a molecular engineering point of view, one of the most logical substitutions is the replacement of the halogen acid in L(+) glutamic acid hydrochloride with one of the other halogen acids. In this paper we report on some of the crystallographic, thermodynamic, linear optical, and nonlinear optical properties of the hydrochloride, hydrobromide, hydroiodide, and mixed crystals of the hydrochloride and hydrobromide salts of L(+) glutamic acid. These data show the effects of halide substitution on the macroscopic linear and first nonlinear polarizabilities.

Experimental

The L(+) glutamic acid halogen acid salts were synthesized by reacting aqueous solutions of L(+) glutamic acid (Atomergic) with the corresponding halogen acid (BDH) at a pH of about 0.4 (20°C). The crystals were then recrystallized at least once from water. Single crystals were grown either by isothermal evaporation (40°C) or the temperature-lowering method (40–25°C).

Mixed crystals of the hydrochloride and hydrobromide were prepared in the following ratios: 85 : 15, 50 : 50, and 75 : 25, by directly mixing the component halogen acid salts. Single crystals were grown from aqueous solution by isothermal evaporation at 40°C.

In order to ascertain the composition of the resulting crystals, the following procedure was employed. A known amount of crystals was

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dissolved in an appropriate quantity of water and the pH adjusted to ~4.0 with aqueous NaOH so that the halide concentration was of the order of 1000 ppm. The chloride and bromide concentrations were then measured by specific ion electrodes correcting for the dilution factors.

Single crystals of the molecular salts with typical dimensions of 0.3 to 0.5 mm on an edge were selected for X-ray analysis. The hydrochloride was investigated using the Pailred single-crystal diffractometer (*3*) with MoKα radiation. The hydrobromide, $HCl_{0.506}HBr_{0.494}$, and hydroiodide were studied using a 10-cm Buerger precession camera with Mo radiation. A 0.2-mm collimator combined with the large 10-cm sample to film distance, produced excellent precession diagrams which led to accurate cell data.

The optical activity in solution was measured with a Rudolph Model 51 polarimeter in 200-mm tubes. Measurements made on aqueous solutions containing 6 wt% of the salt at 20°C using the sodium D line and are considered accurate to 0.05° arc.

Refractive index measurements were made at 5300 ± 50 Å by oil immersion methods at room temperature and are accurate to ±0.004.

Optical second harmonic powder analysis using 1.06-μm radiation was performed with a second harmonic analyzer (*4*) as previously described (*1, 5*). The second harmonic generation (SHG) signal is reproducible to ±10% with a standard deviation of 30%.

Differential thermal analysis (DTA) data were obtained at heating and cooling rates of 10°C min^{-1} under static conditions as described before (*1*).

The specific heats of the crystals were measured with a Perkin–Elmer differential scanning calorimeter, model DSC-2, equipped with an Autoscan Zero interfaced with a Textronix, model 31, minicomputer. Single crystal samples weighing on the order of 10 mg were measured with a precision of ±0.001 mg. Heating rates of 10°K min^{-1} were employed. The calibration of the instrument sensitivity was made by comparing the measured values of the specific heat of sapphire, under identical operating parameters, with the NBS values (*6*). Data points were recorded at 0.46°K intervals between 315 and 425°K, inclusively. The specific heats are estimated to be accurate to ±0.0005 cal g^{-} °K^{-1}.

The optical transmission curves were determined with a Beckman DK-2 UV-Vis spectrophotometer on 2.86-mm thick (001) crystals. The crystal plates were polished flat to 5λ and parallel to 40 arcsec.

Results and Discussion

I. Crystallographic Properties

L(+) glutamic acid hydrochloride crystallizes in a tetramolecular cell in the orthorhombic space group $P2_12_12_1$ (D_2^4) (*7–9*). Precession diagrams for the hydrobromide and the hydroiodide revealed no systematic absence among the (*hkl*), (*hk*0), (*h*0*l*), and (0*kl*) reflections. On the central lines (*h*00), $h = 2n$ only; (0*k*0), $k = 2n$ only; and (00*l*), $= 2n$ only, indicating the unique space group $P2_12_12_1$ (D_2^4).

The hydrobromide has the identical orthorhombic bisphenoidal habit morphology as the hydrochloride (*1*) with the characteristic (100) cleavage. This (100) cleavage is probably a consequence of the van der Waals interaction in the [001] direction (*7*). The hydroiodide has a greater number of facets than the other halide salts with no distinct (100) cleavage indicating a different molecular spatial arrangement.

The crystallographic data for the three isostructural halide salts and the $HCl_{0.506}HBr_{0.494}$ salt are shown in Table II. The refined lattice parameters for the hydrochloride are taken from an earlier work (*5*) and are given for comparative purposes. They are the same as Dawson's (*7*) but are switched for convenience in describing the morphology (*1*). The lattice parameters reported here for the hydrobromide have a greater accuracy than

TABLE I

CHEMICAL ANALYSES OF L(+) GLUTAMIC ACID HYDROCHLORIDE–HYDROBROMIDE MIXED CRYSTALS

	Cl		Br		
Solution composition	Calcd	Found	Calcd	Found	k
$HCl_{0.850}HBr_{0.150}$	16.29	16.39	6.38	6.32	1.006
$HCl_{0.500}HBr_{0.500}$	8.86	8.97	19.66	19.58	1.012
$HCl_{0.250}HBr_{0.750}$	4.20	4.24	27.98	27.92	1.010

TABLE II

SINGLE-CRYSTAL X-RAY DATA FOR L(+) GLUTAMIC ACID SALTS AT 22°C

		Hydrochloride	$HCl_{0.506}HBr_{0.494}$	Hydrobromide	Hydroiodide
Lattice parameters (Å)	a_0	11.737 ± 0.004	11.746 0.009	11.755 ± 0.009	11.506 ± 0.009
	b_0	13.299 ± 0.004	13.338 0.009	13.360 ± 0.009	13.440 ± 0.009
	c_0	5.1404 ± 0.0004	5.249 0.009	5.365 ± 0.009	5.990 ± 0.009
Cell volume (Å^3)		802.37	822.73	843.12	926.30
ρ_x (g cm^{-3})		1.519	1.618	1.796	1.972
ρ_M (g cm^{-3})		1.525 ± 0.005	1.620 0.005	1.805 ± 0.005	1.985 ± 0.005

those previously reported by Dawson and Mathieson (*10*) but are not in good agreement. Their experimental density, however, agrees very well with our X-ray and experimental densities.

Substitution of bromide for chloride increases the c_0 direction by about 4% while the a_0 and b_0 directions increase by 0.15 and 0.5%, respectively. In fact, the cell volume of the hydrobromide is within 5% of the hydrochloride and this increase can be explained by the difference in the ionic radii of four bromines (4 × 1.96 Å), compared to four chlorines (4 × 1.81 Å), inducing rather small changes in bond distances. It appears that the molecular spatial arrangement of both salts is similar and that the relative bond geometry is nearly the same. In support of this conclusion, we observe that the hydrochloride and hydrobromide apparently form a continuous series of solid solutions obtained at a temperature of 40°C, and that the segregation coefficient, k, for bromide in chloride is close to unity (Table I). X-Ray powder diffraction data on mixed crystals of varying composition verified this conclusion.

The situation for the hydroiodide is considerably different. Compared to the hydrochloride and hydrobromide, the a_0 direction is considerably smaller (~0.2 Å) while the c_0 direction is significantly larger (>0.6 Å). A systematic increase is observed only in the b_0 direction. These data indicate that the molecular spatial arrangement of the hydroiodide is probably different.

II. Thermal Properties

DTA studies in air using heating and cooling rates of 10°C min^{-1} shows the hydrochloride, hydrobromide, and hydroiodide salts of L(+) glutamic acid to decompose at 202, 205, and 180°C, respectively. This strongly suggests that the molecular bonding energies of the hydrochloride and hydrobromide are similar while the bonding in the hydroiodide is weaker. Previous work (*1*) on the hydro-

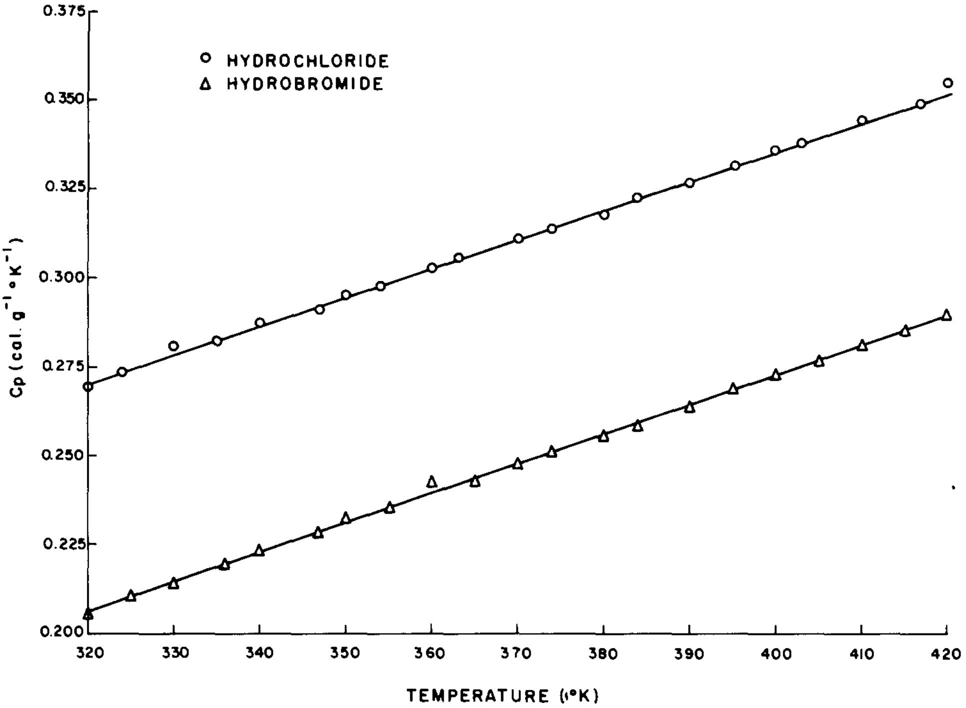

FIG. 1. Temperature dependence of the specific heat of L(+) glutamic acid hydrochloride (O) and hydrobromide (△).

chloride showed the absence of any phase transitions down to −160°C. During the course of this work, no transitions were detected in either the hydrobromide or hydroiodide salts from −30°C to the decomposition point.

The specific heats, at a constant pressure of 1 atm, of the hydrochloride and hydrobromide are shown in Table III. Figure 1 is a graphical representation of these data. The specific heat of the hydrochloride is typically about 25% larger than the hydrobromide. However, the molar heat capacity of the hydrochloride, 54.14 ± 0.09 cal mole^{-1} °K^{-1}, and of the hydrobromide, 52.50 ± 0.12 cal mole^{-1} °K^{-1}, both at 350°K are found to be similar.

Using a least-squares-curve fit, the temperature dependence of the specific heat in the range $320 \leq T\,(°\mathrm{K}) \leq 420$ is found to be

$$C_p\,(\mathrm{cal\ g^{-1}\ °K^{-1}}) = 3.880(10^{-3}) + 8.305(10^{-4})\,T \quad (1)$$

for the hydrochloride and

$$C_p(\mathrm{cal\ g^{-1}\ °K^{-1}}) = -5.994(10^{-2}) + 8.285(10^{-4})\,T \quad (2)$$

for the hydrobromide. One should note that the slopes of both functions are virtually

TABLE III

SPECIFIC HEATS AT CONSTANT PRESSURE OF L(+) GLUTAMIC ACID HYDROCHLORIDE AND L(+) GLUTAMIC ACID HYDROBROMIDE

T (°K)	Hydrochloride C_p (cal g^{-1} °K^{-1})	Hydrobromide C_p (cal g^{-1} °K^{-1})
320.0	0.2688 ± 0.0005	0.2059 ± 0.0005
330.0	0.2786	0.2136
340.0	0.2874	0.2219
350.0	0.2949	0.2302
360.0	0.3028	0.2396
370.0	0.3121	0.2480
380.0	0.3180	0.2553
390.0	0.3270	0.2640
400.0	0.3343	0.2707
410.0	0.3436	0.2785
430.0	0.3555	0.2903

TABLE IV

LINEAR OPTICAL PROPERTIES OF L(+) GLUTAMIC ACID SALTS[a]

	Hydrochloride	$HCl_{0.506}HBr_{0.494}$	Hydrobromide	Hydroiodide
n_x (001)	1.554	1.564	1.574	1.576
n_y (100)	1.566	1.574	1.588	1.596
n_z (010)	1.590	1.598	1.604	1.614
$n_z - n_x$	0.036	0.034	0.030	0.038
$[\alpha]_D^{20}$	+22.9	—	+19.2	+16.3
$[M]_D^{20}$ (10^{-21})	+2.33	—	+2.42	+2.47

[a] Refractive indices at 5300 Å and 20°C.

identical. These data are supportive of similar lattice energies in both the hydrochloride and hydrobromide.

III. Optical Properties

Some of the linear optical properties of the halogen acid salts of L(+) glutamic acid are shown in Table IV. The refractive indices of each salt increase with a corresponding increase in the ionic radii of the halide. The mixed crystal has refractive indices intermediate between the hydrochloride and hydrobromide as would be expected. In order to estimate the atomic contribution by the halide to the refractive index, we utilize the Gladstone–Dale relation (*11*),

$$n = \rho \sum_i P_i k_i + 1, \qquad (3)$$

where ρ is the crystal density and P_i the weight percentage of the specific refractive energy k_i of the component. Larsen and Berman's (*12*) k_i values (Cl = 0.303, Br = 0.214, and I = 0.226) yield the corresponding halide contributions to the refractive index of 0.089, 0.135, and 0.206, respectively. The observed difference between the refractive indices of the halide salts is lower than predicted, particularly for the hydroiodide. The refractive index of the hydrobromide is calculated to be 0.04 larger than the hydrochloride and 0.07 less than the hydroiodide while we observe differences of 0.02 and 0.006, respectively.

The optical activities for aqueous solutions containing 6 wt% of the salt are shown in Table IV also. the specific rotation $[\alpha]$ shows a decrease instead of the expected increase with an increase in the ionic radii of the halide. However, the molecular contribution $[M]$, assuming additivity, shows the correct trend. Here again, as with the refractive indices, the increase is considerably less than might be anticipated.

Table V shows the results of the SHG experiments. Powder data shows all the salts to be phase matchable with average coherence lengths of about 25 μm. The SHG intensity, $d^{2\omega}$, is taken relative to an α-SiO_2 standard and is identical, within ±10% for the hydrobromide, hydrochloride, and the mixed crystals while the hydroiodide is a factor of 3 lower. This is consistent with our other data, which show that the bond geometry of the hydroiodide is different from the other two halide salts.

The optical transmission curves for 2.9-mm-thick (001) crystal plates of the hydrochloride

TABLE V

NONLINEAR OPTICAL PROPERTIES OF L(+) GLUTAMIC ACID SALTS AT 25°C

	Particle size (μm)	$\bar{n}$ (5300 Å)	$d^{2\omega}$ rel α-SiO_2
Hydrochloride	212–300	1.558	1.00
$HCl_{0.506}HBr_{0.494}$	212–300	1.572	1.03
$HCl_{0.253}HBr_{0.747}$	212–300	1.578	1.00
Hydrobromide	212–300	1.584	1.01
Hydroiodide	212–300	1.600	0.33

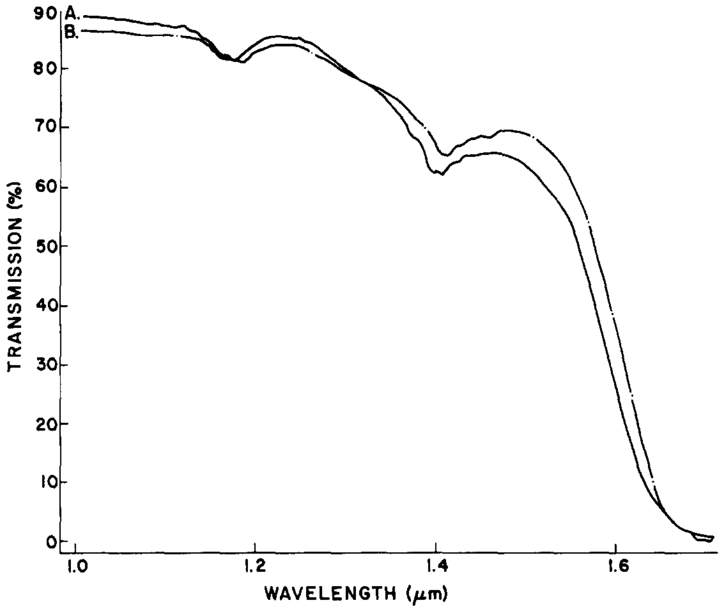

FIG. 2. Infrared transmission curve for 2.9-mm-thick (001) crystal plates of L(+) glutamic acid. (A) hydrochloride (B) hydrobromide.

and hydrobromide salts are shown in Fig. 2. Broad absorption bands are observed at about 1.18 and 1.41 μm for the hydrochloride with a slight shift upon bromide substitution. The transmission goes to zero for both crystals at 1.71 μm.

The band edge at 235.5 nm for the hydrochloride shifts to 237.0 nm for the hydrobromide. This small increase in the linear polarizability is consistent with the other optical data.

IV. Induced Polarization

Crystal structure work on the hydrochloride (*7, 9*) has shown that chlorine is involved in hydrogen bonds of the type OH---Cl and NH---Cl. This is also the case with the hydrobromide and the hydroiodide. But in view of the lack of structural data for these latter salts, specifically of the bond geometry of the rather complex hydrogen bonded system in the latter two compounds, we limit our examination to the macroscopic polarizabilities.

The macroscopic induced polarization P at frequency 2ω arising from an electric field vector E at frequency ω is given by,

$$\mathbf{P} = \chi_{ij}\mathbf{E} + \tfrac{1}{2}d_{ijk}\mathbf{E}^2 + \ldots, \tag{4}$$

where χ_{ij} and d_{ijk} are the linear and first nonlinear polarizabilities, respectively.

The linear polarizability is related to the refractive index by the relation

$$\chi_{ij} = (n_{ij}^2 - 1)/(4\pi) \tag{5}$$

so that for our coordinates, the indices transform as $n_x = n_{33}$, $n_y = n_{11}$, and $n_z = n_{22}$.

In contracted notation (*13*) setting $d_{ijk} = d_{ikj}$, the Kleinman condition (*14*) for 222 symmetry has $d_{14} = d_{25} = d_{36}$.

For the case of SHG, the three polarizations may then be written as

$$P_x = \chi_{33}E_x + d_{14}2E_yE_z, \tag{6a}$$

$$P_y = \chi_{11}E_y + d_{25}2E_xE_z, \tag{6b}$$

$$P_z = \chi_{22}E_z + d_{36}2E_xE_y. \tag{6c}$$

Our values for χ_{ij} are obtained from the refractive index measurements, and the SHG powder measurements give relatively accurate values for d_{ijk} by taking it to be the square root of the second harmonic intensity, $d^{2\omega}$. Here we consider refractive index differences to be negligible and assume similar angle phase matching conditions. Small differences in the phase matching angles and beam walk-off angles are readily shown to be negligible in this somewhat crude approximation. For the L(+) glutamic acid halogen acid salts, the following trends emerge,

$$\chi_{11}, \chi_{22}\text{: I} > \text{Br} > \text{Cl}, \tag{7a}$$

$$\chi_{33}\text{: I} \cong \text{Br} > \text{Cl}, \tag{7b}$$

$$d_{14}, d_{25}, d_{36}\text{: Cl} \cong \text{Br} > \text{I}. \tag{7c}$$

In general, the linear polarizability increases as the ionic radii of the halide increases. This behavior is quite typical, but one should note, as previously discussed, that the increase in the linear polarizability is less than expected from the specific refractive energy contribution of the halide. This is particularly true of χ_{33} for the hydroiodide Eq. (7b).

In considering the nonlinear polarizability, even on a macroscopic scale, it is necessary that the spatial arrangement between crystals is nearly the same and more importantly that the bond geometry be similar so that differences in the orientational contribution to the total nonlinear polarization can be neglected. Since our data clearly indicate a different molecular spatial arrangement for the hydroiodide, we limit our discussion to the hydrochloride and hydrobromide.

As in previous reports (*5, 15*) we ascribe the optical nonlinearity to the nonlinear polarizability of the hydrogen bonds due to the inherent anharmonicity of these bonds. It is assumed that the hydrogen bonds are primarily ionic in character, the degree of ionicity increasing with an increase in the hydrogen bond distance. In terms of electronegativities alone, the hydrobromide hydrogen bonds, i.e., OH---Br and NH---Br, are about 90% as ionic as the hydrochloride hydrogen bonds, i.e., OH---Cl and NH---Cl, but the bromide hydrogen bonds are somewhat longer. We therefore neglect any differences in ionicity of the two compounds. In keeping with these assumptions, the key difference between the hydrochloride and hydrobromide is that the OH---Cl and NH---Cl bonds compared to the OH---Br and NH---Br have a lower reduced mass and are presumably slightly shorter with a similar bond angle. Other bonds of the type OH---O and NH---O differ only in bond distance affected by differences in bond geometry of the halide hydrogen bonds. Our X-ray and optical data indicate a rather small increase in the bond distance of these bonds between hydrochloride and hydrobromide. If we separate the nonlinear polarizability into purely electronic and vibrational contributions, we note that the vibrational character of the bond is perturbed and to a lesser extent, the electronic character. Having shown the optical nonlinearity to be the same in both the hydrochloride and hydrobromide, we conclude that the nonlinear polarizability contribution is primarily electronic since the electron distributions are probably very similar.

This conclusion is consistent with similar observations on the effect of deuterium substitution on the optical nonlinearity in L(+) glutamic acid hydrochloride (*5*) and the hydrazonium tartrate enantiomers (*15*). Admittedly, the deuterium effects are more convincing since bond distances and linear optical properties were completely unaffected. We therefore conclude that isoelectronic substitution in ionic type bonds will not affect the nonlinear polarizability of the bond provided that the bond geometries are similar. In this way, we explain the anomalous behavior of the hydroiodide, since the molecular spatial arrangement is shown to be different. However, this conclusion is not supportive of Miller's rule (*16*) which basically states that an increase in χ_{ij} will be reflected by an increase in d_{ijk}. The Miller tensor neglects the orientational contribution of the individual nonlinear bond polarizabilities to the total nonlinear optical polarization. It cannot account for our observations on the L(+) glutamic acid salts, especially for the behavior of the hydroiodide, although the predicted d_{ijk} values are well within the order of magnitude of its validity.

Summary

The effects of halide substitution in L(+) glutamic acid halogen acid salts have been studied. The hydrochloride, hydrobromide, and hydroiodide are isostructural and the hydrochloride and hydrobromide form solid solution crystals with a segregation coefficient near unity. Single-crystal X-ray analysis, specific heat curves, refractive index measurements, and second harmonic generation experiments indicate similar interatomic bonding in the hydrochloride and hydrobromide but different bond geometries in the hydroiodide. The linear polarizability follows the expected trend I > Br > Cl but the first nonlinear polarizability follows the trend Cl = Br > I. The anomalous behavior of the hydroiodide is attributed to a difference in the orientational contribution to the polarization.

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