

## **DFT Study of NMR Shielding Tensors and Thermodynamic Properties on Pyrene and its Derivatives**

R. Zhiani<sup>1</sup>, M. Anary Abbasinejad<sup>2</sup>, M. Tabatabaee<sup>2</sup> and F.Mollaamin<sup>3,\*</sup>

<sup>1</sup> Ph. D. Student, Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

<sup>2</sup> Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

<sup>3</sup> Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran

### **ABSTRACT**

Emissions from fossil fuel combustion pose a serious threat to public health and impose the need for an improved monitoring of polycyclic aromatic hydrocarbons (PAHs), a major class of persistent organic pollutants. For this purpose the present study reports an investigation of the electronic structure of Pyrene by use of different chemical models. We also made a comparison between different chemical models.

Donor – acceptor disubstituted, entropy, enthalpy and Gibbs free-energy will be compared too.

The isotropic and anisotropic tensor of the pyrene and derivatives structure were calculated with different chemical models HF/6-31G, HF/6-31G\*, BLYP/6-31G, BLYP/6-31G\*, B3LYP/6-31G, B3LYP/6-31G\* and as well.

**Keywords:** PAHs, Pyrene; Isotropic; Anisotropic; Chemical models

### **INTRODUCTION**

Polycyclic aromatic hydrocarbons (PAHs) are the products of thermal decomposition, forming during incomplete combustion of organic materials and geochemical formation of fossil fuels in power plants, domestic heating, waste incineration, industrial processes and, most importantly, motor vehicle exhaust [1-3].

Carcinogenic, mutagenic and immunotoxic effects of PAHs detrimental to human health have been reported frequently. Regulation of PAHs emission and reliable monitoring of PAHs concentration in ambient air is thus of paramount importance for public health. Motor vehicle exhaust is considered the most significant source for PAHs in urban areas.

Geochemical processes yield PAHs when natural organic matter (NOM) is exposed to high pressure and temperature.

These compounds can be point source pollutants (e.g. oil spill) or non point source (e.g. atmospheric deposition) and are one of the most widespread organic pollutants.

Anthropogenic practices, such as industrial processing, petroleum spills, and incomplete combustion of fuel, also contribute to high levels of PAHs in the environment [4,5].

Pyrene is a polycyclic aromatic hydrocarbon (PAHs) consisting of four fused benzene rings, resulting in a large, flat aromatic system. Pyrene forms during incomplete combustion of organic materials. Animal studies have shown that pyrene is toxic to the kidneys and the liver. Pyrene has wide spread of applications, from making pharmaceuticals, and plastics to being a valuable molecular probe for fluorescence spectroscopy or a probe to determine solvent environments.

### **THEORETICAL BACKGROUND**

The chemical shielding refers to the phenomenon which is associated with the secondary magnetic field created by the induced motions of the electrons that surrounding the nuclei when in

\*Corresponding author: smollaamin@gmail.com

the presence of an applied magnetic field [6]. The energy of a magnetic moment  $\eta$ , in a magnetic field,  $B$ , is as follow

$$E = -\eta (1 - \sigma) B \quad (1)$$

where the shielding  $\sigma$ , is the differential resonance shift due to the induced motion of the electrons. The chemical shielding is characterized by a real three-by-three Cartesian matrix, which can be decomposed into a single scalar term, three antisymmetric pseudo vector components, and five components corresponding to a symmetric tensor [7]. Only the single scalar and the five symmetric tensor elements can be observed in the normal NMR spectra of the solids. For brevity, these six values are usually referred to as the shielding tensor:

$$\begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \quad (2)$$

That can be obtained by averaging the off-diagonal values of the complete tensor [8].

The chemical shielding tensor is commonly referred to the chemical shift anisotropy (CSA) tensor according to the possession of second rank properties. The measurement or calculation of the diagonal components ( $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ ) or ( $\sigma_{11}, \sigma_{22}, \sigma_{33}$ ) in the principle axis system (PAS) allows the complete description of the CSA tensor [sandia]. The CSA tensor can also be described by three additional parameters.

a) The isotropic value (or trace portion of the CSA tensor)  $\sigma_{iso}$ , of the shielding tensor which

$$\text{is defined as } \sigma_{iso} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (3)$$

b) The anisotropy ( $\Delta\sigma$ ) of the tensor, due to the following expression:

$$\Delta\sigma = \sigma_{33} - \frac{1}{2} (\sigma_{11} + \sigma_{22}) \quad (4)$$

c) The shielding tensor asymmetry parameter ( $\eta$ ) which is given by:

$$\text{and } \eta = \frac{|\sigma_{22} - \sigma_{11}|}{|\sigma_{33} - \sigma_{iso}|} \quad (5)$$

#### COMPUTATIONAL METHODS

In the present work, we have optimized isolated molecule with 6-31G and 6-31G\* basis sets in the gas phase. All calculations were done with

the Gaussian 98 package [9,10] at the Hartree-Fock (HF) level of theory and Density Functional Theory (B3LYP and BLYP) [11,15].

#### RESULTS AND DISCUSSION

The geometry optimization for pyrene and its derivatives structures have been obtained with HF, BLYP and B3LYP methods with 6-31G and 6-31G\* basis set are shown in Fig 1.

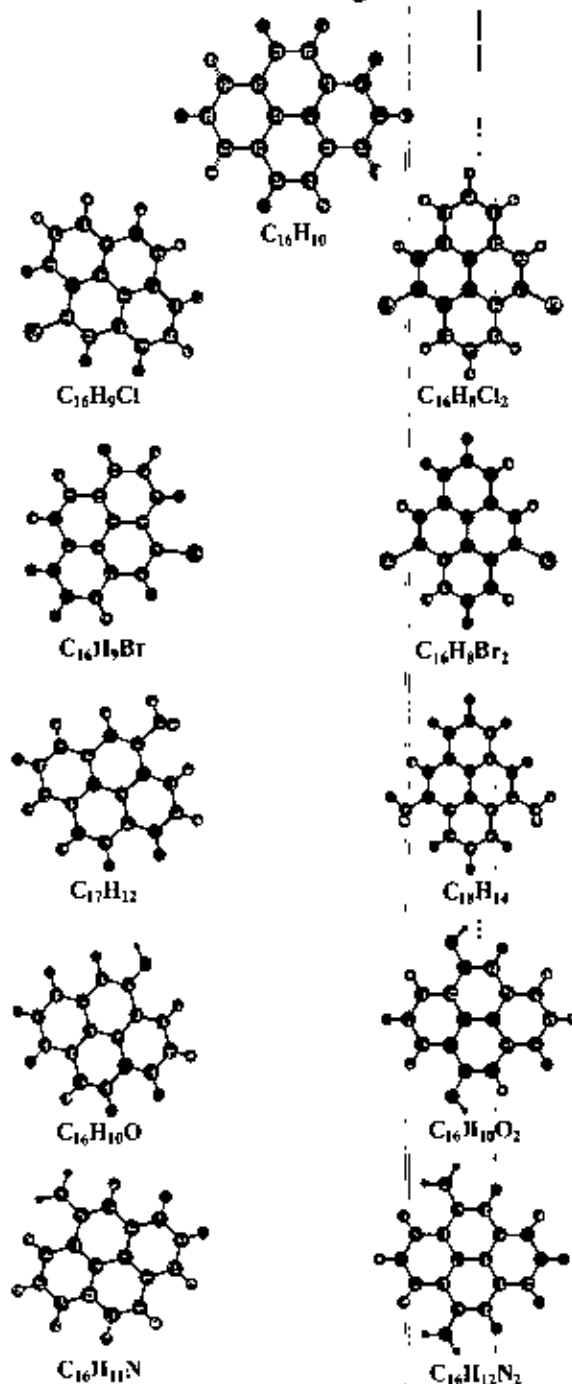


Fig. 1. Optimized configuration of pyrene and its derivatives.

The results obtained for thermodynamic properties in gas phase at 298.15 K for pyrene and its derivatives based on DFT calculations at three methods and two sets are shown in the following tables.

A comparison of Entropy (S) and Gibbs free-energy (G) and Enthalpy (H) are obtained for different basis sets and for one-substituted pyrene that is summarized in table 1.

Table 2 has also shown the results obtained for the two-substituted pyrene.

As shown in table 1, the maximum values for Enthalpy (H) and Gibbs free-energy (G) was obtained when 6-31G\* basis set level used at B3LYP method.

It is also clear in Table (1) and (2) all the values obtained for (H), (G) and (E) using all the methods are negative for pyrene derivatives with electron-drawing groups than those with electron-releasing groups. These values are also more negative for bi-substituted pyrenes than for one-substituted pyrene (Table 1, 2).

Studying the entropy values for different pyrene derivatives, made it clear that 6-31G\* basis set gave the largest values among the other used sets. Considering the optimized structure, we also calculated the NMR shielding tensors. The isotropic and anisotropic values calculated for these structure with different chemical models are presented in Fig. 2 and 3.

Table1. Optimized parameters at theoretical level of relative stability energies (E) electronic and thermal enthalpy (H), entropy (S), Gibbs free-energy (G) at 298.15 K

Structure	method	Basis set	-H (Electronic and thermal kcal/mol <sup>1</sup> )	-G (Electronic and thermal kcal/mol <sup>1</sup> )	S (Electronic and thermal kcal/mol <sup>1</sup> K <sup>-1</sup> )	-E (Electronic and thermal kcal/mol <sup>1</sup> )
C <sub>16</sub> H <sub>10</sub>	HF	6-31G	383609.2317	383637.1189	0.09353	383609.8241
	BLYP	6-31G	386019.3702	386048.5569	0.09790	386019.9626
	B3LYP	6-31G	386178.2418	386207.0389	0.09790	386178.8348
C <sub>16</sub> H <sub>10</sub>	HF	6-31G*	383744.3237	383772.5003	0.04479	383744.4156
	BLYP	6-31G*	386099.1524	386128.5136	0.09848	386099.7440
	B3LYP	6-31G*	386266.2858	386295.278	0.09724	386266.878
C <sub>16</sub> H <sub>9</sub> Cl	HF	6-31G	671564.0686	671593.3965	0.09837	671713.0538
	BLYP	6-31G	674405.8345	674437.2256	0.10587	674406.4268
	B3LYP	6-31G	674671.4385	674671.5431	0.10440	673566.9248
C <sub>16</sub> H <sub>9</sub> Cl	HF	6-31G*	671712.4614	671742.6252	0.10117	671713.0538
	BLYP	6-31G*	674497.4439	674528.9506	0.10567	674498.0362
	B3LYP	6-31G*	674702.6013	674702.5059	0.10460	674672.0202
C <sub>16</sub> H <sub>9</sub> Br	HF	6-31G	1995799.493	1995830.045	0.10250	1995800.086
	BLYP	6-31G	1999339.970	1999373.0212	0.1110	1999340.563
	B3LYP	6-31G	1999664.063	1999695.869	0.10668	1999664.655
C <sub>16</sub> H <sub>9</sub> Br	HF	6-31G*	1996013.687	1996044.593	0.10366	1996014.279
	BLYP	6-31G*	1999342.937	1999374.965	0.10742	1999343.529
	B3LYP	6-31G*	1999664.063	1999695.869	0.10668	1999664.655
C <sub>17</sub> H <sub>12</sub>	HF	6-31G	408075.3163	408105.1224	0.01000	408075.9087
	BLYP	6-31G	410650.3154	410681.6664	0.10515	410650.9078
	B3LYP	6-31G	410681.6549	410681.6664	0.10115	410826.185
C <sub>17</sub> H <sub>12</sub>	HF	6-31G*	408250.3875	408250.49	0.10241	408220.9776
	BLYP	6-31G*	410735.5054	410767.0271	0.10573	410736.0978
	B3LYP	6-31G*	410919.7491	410950.836	0.10427	410920.342
C <sub>19</sub> H <sub>10</sub> O	HF	6-31G	430558.299	430587.6853	0.09856	430558.8911
	BLYP	6-31G	433196.5648	433227.3278	0.10318	433197.1571
	B3LYP	6-31G	433358.0807	433388.4145	0.10174	433358.672
C <sub>16</sub> H <sub>10</sub> O	HF	6-31G*	430713.292	430742.9776	0.09957	430713.8842
	BLYP	6-31G*	433291.1186	433322.0655	0.10380	433291.710
	B3LYP	6-31G*	433462.1802	433492.7217	0.10244	433462.772
C <sub>16</sub> H <sub>11</sub> N	HF	6-31G	418118.1651	418143.3970	0.0980	418114.7543
	BLYP	6-31G	420723.6482	420754.1879	0.1024	420724.2406
	B3LYP	6-31G	420891.9946	420922.0567	0.1008	420892.5870
C <sub>16</sub> H <sub>11</sub> N	HF	6-31G*	418259.8288	418289.8357	0.1006	418260.4218
	BLYP	6-31G*	420811.5372	420842.7088	0.1045	420812.1240
	B3LYP	6-31G*	420988.7867	421019.5497	0.1032	420989.3907

**Table 2.** Optimized parameters at theoretical level of relative stability energies (E) electronic and thermal-enthalpy (H), entropy (S), Gibbs free-energy (G), at 298.15 K

Structure	method	Basis set	-H (Electronic and thermal kcal/mol <sup>-1</sup> )	-G (Electronic and thermal kcal/mol <sup>-1</sup> )	S (Electronic and thermal kcal mol <sup>-1</sup> K <sup>-1</sup> )	-E (Electronic and thermal kcal/mol <sup>-1</sup> )
C <sub>16</sub> H <sub>10</sub>	HF	6-31G	383609.2317	383637.1189	0.09353	383609.8241
	BLYP	6-31G	386019.3702	386048.5569	0.09790	386019.9626
	B3LYP	6-31G	386178.2418	386207.0389	0.09790	386178.8348
C <sub>16</sub> H <sub>8</sub> Cl <sub>2</sub>	HF	6-31G	959548.9227	959549.0322	0.10922	959517.7364
	BLYP	6-31G	962791.7597	962825.3684	0.11270	962792.352
	B3LYP	6-31G	962963.0271	962996.0887	0.11889	962963.6201
C <sub>16</sub> H <sub>8</sub> Cl <sub>2</sub>	HF	6-31G*	959680.1446	959712.2938	0.10780	959680.737
	BLYP	6-31G*	962895.3709	962929.023	0.11287	962895.9633
	B3LYP	6-31G*	963076.2822	963109.3617	0.11120	963076.7946
C <sub>16</sub> H <sub>8</sub> Br <sub>2</sub>	HF	6-31G	3607989.275	3608022.47	0.11134	3607989.853
	BLYP	6-31G	3612666.131	3612730.43	0.21570	3612666.724
	B3LYP	6-31G	3612809.411	3612843.187	0.11305	3612809.481
C <sub>16</sub> H <sub>8</sub> Br <sub>2</sub>	HF	6-31G*	3608282.567	3608316.204	0.11281	3608283.116
	BLYP	6-31G*	3612912.301	3612947.419	0.11779	3612912.894
	B3LYP	6-31G*	3613061.455	3613096.066	0.11608	3613062.044
C <sub>18</sub> H <sub>18</sub>	HF	6-31G	432541.2692	432572.9791	0.10636	432541.8616
	BLYP	6-31G	435281.6791	435314.5932	0.11040	435281.7073
	B3LYP	6-31G	435472.8078	435505.7609	0.11050	435473.4008
C <sub>18</sub> H <sub>14</sub>	HF	6-31G*	432696.3123	432728.3304	0.10739	432696.9047
	BLYP	6-31G*	435371.7129	435405.3556	0.11284	435372.3053
	B3LYP	6-31G*	435573.0738	435606.2157	0.11116	435573.6668
C <sub>16</sub> H <sub>10</sub> O <sub>2</sub>	HF	6-31G	477507.4849	477538.3621	0.10356	477508.0772
	BLYP	6-31G	480373.6809	480406.0717	0.10864	480374.2733
	B3LYP	6-31G	480537.8701	480569.777	0.10702	482420.8573
C <sub>16</sub> H <sub>10</sub> O <sub>2</sub>	HF	6-31G*	477682.3555	4777135.5464	0.10461	477682.9478
	BLYP	6-31G*	480482.9799	480515.5903	0.10937	480483.5723
	B3LYP	6-31G*	480657.9967	480690.1465	0.107831	480658.5897
C <sub>16</sub> H <sub>12</sub> N <sub>2</sub>	HF	6-31G	452618.5342	452649.2495	0.103196	452619.1265
	BLYP	6-31G	455427.1412	455459.1300	0.10802	455427.7335
	B3LYP	6-31G	455605.0232	455636.6415	0.106048	455605.6155
C <sub>16</sub> H <sub>12</sub> N <sub>2</sub>	HF	6-31G*	452778.6419	452810.1969	0.10583	452779.2343
	BLYP	6-31G*	455523.5242	455556.5569	0.1108	455524.0977
	B3LYP	6-31G*	455710.9380	455743.4913	0.10918	455711.5304

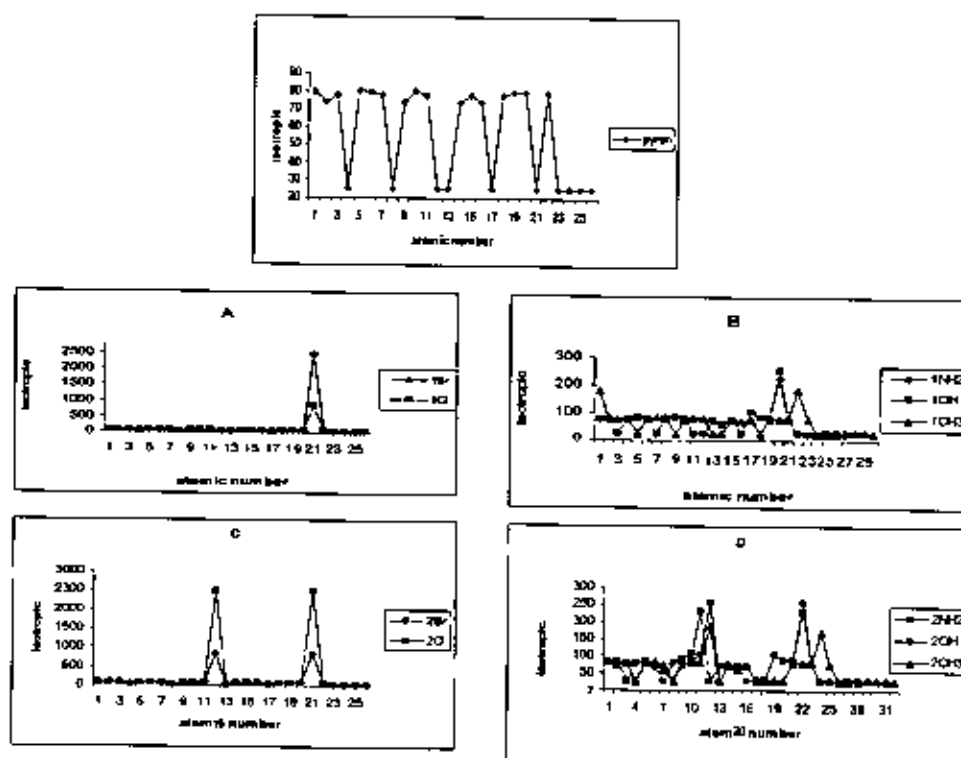


Fig. 2. Comparison between Isotropic Shielding for pyrene and its derivatives.

- A: Comparison between Isotropic Shielding for  $C_{16}H_9Cl$ ,  $C_{16}H_9Br$   
 B: Comparison between Isotropic Shielding for  $C_{16}H_{10}O$ ,  $C_{16}H_{11}N$ ,  $C_{17}H_{12}$   
 C: Comparison between Isotropic Shielding for  $C_{16}H_9Cl_2$ ,  $C_{16}H_8Br_2$   
 D: Comparison between Isotropic Shielding for  $C_{16}H_{10}O_2$ ,  $C_{16}H_{12}N_2$ ,  $C_{18}H_{14}$

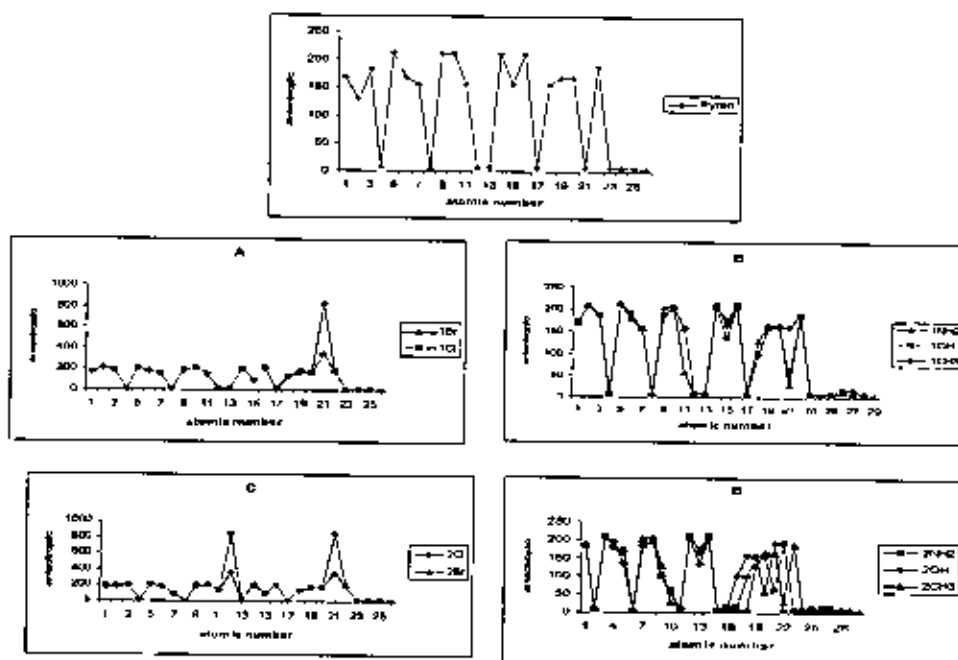


Fig. 3. Comparison between Anisotropic Shielding for pyrene and its derivatives.

- A: Comparison between Anisotropic Shielding for  $C_{16}H_9Cl$ ,  $C_{16}H_9Br$   
 B: Comparison between Anisotropic Shielding for  $C_{16}H_{10}O$ ,  $C_{16}H_{11}N$ ,  $C_{17}H_{12}$   
 C: Comparison between Anisotropic Shielding for  $C_{16}H_9Cl_2$ ,  $C_{16}H_8Br_2$   
 D: Comparison between Anisotropic Shielding for  $C_{16}H_{10}O_2$ ,  $C_{16}H_{12}N_2$ ,  $C_{18}H_{14}$

As shown in Fig. 2 and 3 the largest values are related to the substituent atoms directly connected to the pyrene ring. Meanwhile, the values for electron-withdrawing groups are greater than those for electron-releasing groups. For example the values calculated for hydroxyl, amino and methyl groups are in the order  $\text{OH} > \text{NH}_2 > \text{CH}_3$  (Fig. 2B). This order was also observed for two-substituted pyrenes (Fig 2D). In the case of halogenated pyrenes the values are greater for bromine than chlorine substituent (Fig. 2A, 2C).

It could be related to the better overlap between the 2p orbital of carbon atom and 3p orbital of chlorine atom relative to 4p orbital of bromine atom arising from the smaller size of 3p orbital.

Isotropic diagram indicates that all carbon atoms except the geminal one relative to the substituent have fixed values. This result is also the same for anisotropic field. The geminal carbon atoms relative to the electron-acceptor have the lowest isotropic values, but the neighboring atoms of electron donor substituents have the highest values

(Fig. 2,3). This pattern may be explained on the basis of this fact that the ortho carbons of the aromatic rings get the largest influence from the donor or acceptor substituents.

This pattern can be observed for anisotropic field (see Fig. 2, 3).

## CONCLUSION

The HF, BLYP, B3LYP, 6-31G and 6-31G\* levels of theory of ab initio method have been employed for the study of pyrene and its derivatives. Our present study shows that optimization of structure at the B3LYP/6-31G, 6-31G\* level in the gas phase is suitable for this case. The amount of Enthalpy (H) and Gibbs free-energy (G) for electronegative substituents like bromine and chlorine are more negative than that of electron donor substituent's like methyl and amino groups.

Electronegative groups have more isotropic and anisotropic values.

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