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Theoretical Study of Magnetic Susceptibility and Optical Activity of Small Molecules Containing one Chiral Center

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In the first part of this work, correlation between optical activity and elements of magnetic susceptibility tensor (MST) for five classes of model small molecules containing a single chiral center has been studied using quantum computational techniques at DFT-B3LYP level of theory with 6-311G basis set. Several molecular properties are used to reduce the MST elements prior to the examination of the correlation. This study showed a close correlation between optical activity and the off-diagonal MST elements reduced by the electronic spatial extent $<r^2>$. In the second part of this work, effects of the type of substitutions and their distances from the chiral center on the optical activity of these molecules have been investigated. Results of this work show that optical activity is reduced effectively upon distancing the substitution groups from the chiral center. Furthermore, the set of substitutions with higher electron densities and larger differences in their electronic structures result in higher optical activity.

Keywords: Optical activity, Magnetic susceptibility, Correlation, Electronic spatial extent, Chirality

INTRODUCTION

Ability of some materials in rotating polarization direction of the plane polarized light, known as optical activity, was first observed and reported by Pasteur, almost 160 years ago [1], about 30 years after, Biot reported a work on the plane polarized light and possibility of its changes in some media [2]. Since then, numerous theoretical and experimental works have been carried out to characterize and apply this property. The most interesting feature of this property is that for every optically active compound, there exists a counterpart compound with the same stoichiometry, connectivity and physical properties, but rotating the polarization plane in the opposite direction. The only structural/bonding difference between these two compounds is the handedness of the arrangement of the groups attached to an atomic center; these two compounds are thus called *optical isomers*.

Because of its increasing importance and applications as a research tool in the design and characterization of new molecules and functionalized molecular devices in the construction of nano-actuators, nano-sensors and nano-electronic circuits, especially single-photon and single-electron devices, optical activity has received great attentions and has been used widely to identify and characterize compounds having this property. Some new applications include the modified heterogeneous enantioselective catalysts [3], chiral drugs [4], fiber optics [5], thermal conductive carbon nanotubes [6], chiral gold nano-gratings [7] and molecular devices based on the light-controlled charge carrier mobility [8]. A number of attempts [9-11] have been made to elucidate the detailed physical basis of this phenomenon. In early studies, empirical models, such as Brewster's rule, were used [12], while in more recent studies, theoretical methods are applied [13]. Satisfactory values have been obtained for optical rotation (at the sodium D-lines) for certain molecules based on some theoretical studies [14-15]. In some of the works carried out on optical activity, the tensor components of the optical rotation, and the effect of conformational changes on the

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*Corresponding author. E-mail: sabzyan@sci.ui.ac.ir optical rotation have been studied [9,16-19]. Furthermore, to investigate overall effects of structural changes on the optical rotation, a molecular quantum similarity index has also been introduced based on the electron probability density, and evaluated for enantiomers of molecules containing one or two chiral centers, *i.e.* molecules possessing two asymmetric carbon atoms [20-24]. However, details of different aspects of geometry and electron density effects on the optical rotation have not been worked out yet. Moreover, no simple picture has been reported by which comparative optical activities of different molecules can be estimated even semi-quantitatively.

In the case of solution, liquid and gas phases, which is of our interest in this work, after applying rotational averaging, optical rotation α is given by

$$\alpha = \frac{N^{*} l \omega^{2}}{3\hbar c^{2} \varepsilon_{0}} \sum_{n \neq 0} \frac{\mathrm{Im}[\boldsymbol{\mu}_{0n} \otimes \mathbf{m}_{n0}]}{\omega_{n0}^{2} - \omega^{2}} \tag{1}$$

where $[\boldsymbol{\mu}_{0n} \otimes \mathbf{m}_{n0}]$ is the direct product of the matrix elements of the electric and magnetic dipole moment vector operators $\boldsymbol{\mu}$ and $\mathbf{m}$ ($\boldsymbol{\mu}_{0n} = <\psi_0|\boldsymbol{\mu}|\ \psi_n >$ and $\mathbf{m}_{n0} = <\psi_n|\mathbf{m}|\ \psi_0 >$), ω is the angular frequency of the incident light, $\omega_{no} = (E_n - E_0)$ with $(E_n - E_0)$ being the excitation energy from the electronic ground state ψ_0 to the excited state ψ, N^* is the molecular number density, ι is the optical path length inside the optically active medium, ε_0 is the vacuum permittivity, and c is the speed of light. Equation (1) is valid up to the second-order perturbation theory for non-intense optical sources (*i.e.* in the absence of any non-linearity) [25-28]. The computational and experimental optical rotation is often reported as the specific optical rotation $[\alpha]_D$ based on the frequency of the sodium D-line (*i.e.* 5890-5896 Å) in a cell of unit length.

The first rank magnetic polarization tensor $\boldsymbol{M}$ is related to the magnetic field $\boldsymbol{H}$ *via*

$$\boldsymbol{M} = \chi_m \boldsymbol{H} \tag{2}$$

in which the second rank magnetic susceptibility tensor (MST) χ_m, is a bulk/molecular characteristic determining the induced magnetization of a molecular system in an electromagnetic radiation field. For example, in the case of an isotropic medium exposed to a homogeneous magnetic field, the isotropic part of the molar magnetic susceptibility tensor $\chi_{m,iso}$ is given by perturbation theory as

$$\chi_{m,iso} = -\left(\frac{N_A e^2 \mu_0}{6m_e}\right)\left\langle r^2 \right\rangle + \left(\frac{N_A e^2 \mu_0}{6m_e^2}\right) \sum_{n \neq 0} \frac{\left|L_{0n}\right|^2}{\hbar \omega_{n0}} \tag{3}$$

in which N_A is the Avogadro's number, e and m_e are the charge and mass of electron, μ_0 is the permanent electric dipole moment, $<r^2>$ is the electronic spatial extent, and L_{0n} is the magnitudes of the $|0> \rightarrow |n>$ transition angular momentum [29,30]. The transition angular frequency ω_{0n} is defined above. According to Eq. (3), static molecular characteristics μ_0, ω_{n0} and $<r^2>$, together with the dynamic characteristic L_{0n} determine magnetic susceptibility of a molecule. Eq. (3) also shows that the total molar magnetic susceptibility χ_m can be considered to be composed of two components; a negative diamagnetic susceptibility, χ_m^d (the first term), and a positive paramagnetic susceptibility, χ_m^p (the second term), with $\chi_m = \chi_m^d + \chi_m^p$.

Optical activity of a chiral molecule, as can be seen from Eq. (1), depends on its electric and magnetic properties. Transition angular momentum L_{0n} appearing in Eq. (3) and transition magnetic dipole moment m_{0n} appearing in Eq. (1), are correlated *via* $m_{0n} = -(L_{0n} + g_e s_{0n})\gamma_e$ with $\gamma_e = e/2m_e$ being electron magnetogyric ratio and $g_e = 2.00232$ the electron *g*-factor. For closed shell systems, spin angular momentum is zero and this relation is reduced to $m_{0n} = -\gamma_e L_{0n}$. Furthermore, asymmetry of the distribution of the electron density in the molecule contributes to both optical activity and magnetic susceptibility. Therefore, a close correlation between the magnetic susceptibility χ_m and the specific rotation $[\alpha]_D$ is expected naturally.

COMPUTATIONAL DETAILS AND METHODOLOGY

Structures of the $CX_iY_jZ_k$ (with $i+j+k = 4$, and X,Y,Z = H,F,Cl,Br) and $C(CX_3)_4$ (with X = H,F,Cl,Br) series of molecules have been optimized with hybrid density functional theory (DFT) B3LYP method [31-32] and the 6-311G basis set. Magnetic susceptibility tensor (MST) elements corresponding to these optimized structures are calculated using the GIAO method [33]. These model molecules are selected to demonstrate correlation between the MST diagonal/off-diagonal elements and the symmetry of the molecule.

To investigate correlations between optical activity and the diagonal/off-diagonal elements of the MST, five series of chiral model molecules having non-zero optical rotation are designed (Fig. 1). In each series of molecules, the end groups, which are collectively responsible for chirality, are distanced linearly from the chiral center either by $(Be)_n$ atoms as in the $\mathbf{A}_n$, $\mathbf{B}_n$ and $\mathbf{D}_n$, or by $(\text{-C≡C-})_n$ groups as in the $\mathbf{C}_n$, or by $(\text{=C=})_n$ as in the $\mathbf{E}_n$ types of molecules. Therefore, the notation $\mathbf{M}_n$ is used to denote the model molecule **M** (of **A**, **B**, **C**, **D** or **E** type) having *n* intermediate atoms/groups (Be, -C≡C- or =C=) in each branch. For the **A**, **B**, **C**, and **D** series of molecules, $\mathbf{M}_0$ denotes the first member having no intermediate atom/group. For the **E** series of molecules, $\mathbf{E}_0$ denotes the CHFClBr molecule which has no intermediate =C= group. The $\mathbf{E}_n$ molecules with even values of *n* are planar and do not have optical rotation, and thus are not intended here.

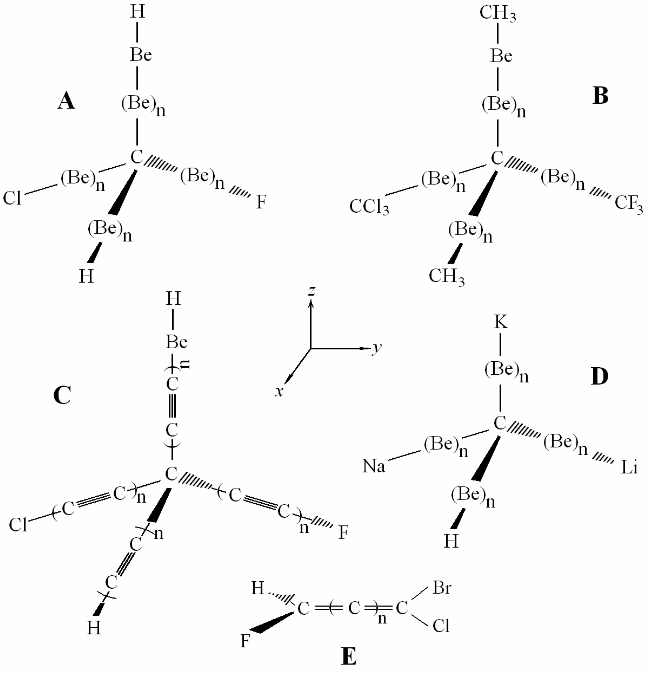

Fig. 1. The five series of model molecules designed in this work to investigate correlation between the magnetic susceptibility tensor elements and optical rotation. The molecular frame used in this report is also demonstrated.

Such selection of the model molecules allows us also to study effect of the distance of the substitutions from the chiral center on the level of optical activity. Structures of these molecules are optimized at DFT-B3LYP/6-311G level of theory. In this optimization, a linear geometry is imposed on the atoms of the stem of each branch to avoid any deviations (however very small) from linearity, so that the effects of the end groups and their distances could be isolated conveniently. Electric charge distribution and geometrical parameters of these optimized structures are extracted, and their specific optical rotations and the GIAO MST elements are calculated. All calculations of this work have been carried out using the G03W program [34].

Present method is based on the comparative trends of the MSA elements and optical rotation values in each molecular series, and between corresponding molecules of different series. Although the computational method and basis set may affect the numerical values of the calculated quantities [35,36], they do not alter observation of correlation between these quantities. Furthermore, the DFT functional used in the present study has worked well for most molecular quantities. More specifically, Polavarapu has shown that DFT-B3LYP method could give acceptable results for optical rotation values [19], and Helgaker *et al.* have mentioned that DFT-B3LYP method can be used for the calculations of the MST elements [37]. The method and basis set used in this study were suitable enough to detect any correlation between the MST off-diagonal elements and optical rotation values. Examination of more advanced methods and larger basis sets can however be interesting and can be carried out in continuation of the present study, which is beyond the scope of the present work.

RESULTS AND DISCUSSION

The GIAO MST elements and electric dipole moments obtained for the $CX_iY_jZ_k$ (with $i+j+k = 4$, and X,Y,Z = H,F,Cl,Br) and $C(CX_3)_4$ (with X = H,F,Cl,Br) molecules are reported in Table 1. As can be seen from these data, the MST can clearly represent the spherical, elliptic and planar symmetries of electron density distribution of the CX_4/$C(CX_3)_4$, CX_3Y and CX_2YZ groups of molecules, respectively with T_d, C_3V, and C_S point groups. Different values obtained for MST elements of different members of the CX_4, CX_3Y and CX_2YZ types of molecules show the distinct difference between the contributions from the X, Y and Z types of atoms. The GIAO MST elements have also been calculated using the same level of theory and the same basis set for the optimized structures of the *R*- and *S*- isomers of the CHFClBr, $C(CH_3)(CF_3)(CCl_3)(CBr_3)$, $C(CH_2H)(CF_2H)(CCl_2H)(CBr_2H)$ and $C(CHH_2)(CFH_2)(CClH_2)(CBrH_2)$ chiral molecules as the prototype asymmetric species. Results of these calculations are reported in the second part of Table 1. For brevity, in this table and in the rest of this article, these four chiral molecules are denoted respectively as C{X}, $C\{(CX_3)\}$, $C\{(CX_2H)\}$ and $C\{(CXH_2)\}$. The isotropic and anisotropic parts of the MST, χ_{iso} and χ_{aniso}, reported in Table 1, are defined, respectively as

$$\chi_{iso} = \frac{1}{3} Tr(\chi_m) = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}),$$
$$\chi_{aniso} = \chi_{33} - \frac{1}{2}(\chi_{11} + \chi_{22}),$$
$$\text{with } \chi_{11} < \chi_{22} < \chi_{33} \tag{4}$$

where $Tr(\chi_m)$denote the trace of the MST matrix, and χ_{ii} ($i = x, y, z$) are its diagonal elements. The anisotropic part of the MST, χ_{aniso}, measures deviation from the reference spherical symmetry.

For spherical molecules, MST has three identical diagonal and all zero off-diagonal elements and thus has no anisotropy, *i.e.* $\chi_{aniso} = 0$. For cylindrical and elliptical molecules, two of the diagonal elements of MST are identical, and two of the off-diagonal elements are non-zero due to symmetry requirements. As expected, due to their spherical or cylindrical symmetries, values of the off-diagonal elements of MST are all zero for the achiral $C(CX_3)_4$, CX_4, CXY_3 and CX_2Y_2 molecules. While, for the $C\{(CX_3)\}$ and $C\{(CX_2H)\}$ groups of chiral molecules (Table 1b), MST has non-zero off-diagonal elements χ_{ij} and non-zero anisotropy χ_{aniso}. Analysis of the calculated values of the reduced anisotropic part of MST, defined as $\bar{\chi}_{aniso} = \chi_{aniso}/\chi_{iso}$, for non-spherical molecules shows the following trends for the CXY_3, CX_2Y_2 and CX_2YZ series of molecules.

$$\bar{\chi}_{aniso}(CXY_3): \quad CHBr_3 > CHCl_3 > CFBr_3 > CFCl_3 > CClBr_3 > CHF_3 \tag{5a}$$

$$\bar{\chi}_{aniso}(CX_2Y_2): \quad CF_2Br_2 > CH_2Br_2 > CH_2Cl_2 > CF_2Cl_2 > CH_2F_2 > Cl_2Br_2 \tag{5b}$$

$$\bar{\chi}_{aniso}(CX_2YZ): \quad CCl_2BrF > CF_2HCl > CBr_2FCl > CCl_2HF > CCl_2HBr > CBr_2HCl > CF_2HBr > CH_2ClF > CH_2BrF > CBr_2HF > CF_2BrCl > CH_2BrCl \tag{5c}$$

These trends can be attributed to the differences in the number of active electrons of the X and Y atoms, and therefore, to the differences in the extent of asymmetry of the electron density around the central atom C.

The most interesting feature of the calculated MSTs is that for the pair of optical isomers of each chiral molecule, the absolute numerical values of the corresponding diagonal and off-diagonal elements of the MST are exactly equal but at least two corresponding pairs of the off-diagonal elements have opposite signs. A comparative analysis shows that the numerical values of both diamagnetic and paramagnetic MST elements increase with the number of X atoms in the $C\{(CX_nH_{3-n})\}$ (with n = 1-3) series of molecules. This trend clearly shows that asymmetry of the electron density around the chiral center increases with increasing number of active electrons of the (CX_nH_{3-n}) groups.

Almost the same trends as described above are observed for the values of the MST elements calculated with all (GIAO [33], IGAIM [38,39] and CSGT [39]) methods available for calculating magnetic properties. Because of providing the best correlation with the calculated optical rotation values, only the GIAO MST elements are reported and discussed here.

Correlation Between Optical Activity and Magnetic Susceptibility

In this section, existence of possible correlation between molecular optical rotation and magnetic susceptibility tensor (MST) elements is investigated first, and then effects of substitutions and their distances to the chiral center on the values of the optical rotation and MST elements, and their

Table 1. (a) The GIAO Diamagnetic and Paramagnetic Parts of the Magnetic Susceptibility Tensor (MST) Elements (in au) Calculated for the CX_4, CX_3Y, CX_2Y_2, CX_2YZ and $C(CX_3)_4$ Types of Molecules (with X,Y = H, F, Cl, Br) Obtained at B3LYP/6-311G Level of Theory. For these T_d, C_{3V} or C_{2V} Symmetric Molecules, all Off-Diagonal Elements of MST are Zero

Symmetric molecule	Diamagnetic			Paramagnetic		
	$-\chi_{xx}$	$-\chi_{yy}$	$-\chi_{zz}$	χ_{xx}	χ_{yy}	χ_{zz}
CH_4	5.98	5.98	5.98	1.91	1.91	1.91
CF_4	50.12	50.12	50.12	42.99	42.99	42.99
CCl_4	160.05	160.05	160.07	145.51	145.52	145.53
CBr_4	361.9	361.92	361.93	342.66	342.69	342.7
CH_2F_2	12.2	29.13	32.76	7.22	24.46	28.43
CH_2Cl_2	21.6	86.7	93.41	9.86	76.17	84.29
CH_2Br_2	27.31	192.08	200.29	11.34	177.95	188.01
CF_2Cl_2	72.05	106.15	122.12	59.68	95.13	111.82
CF_2Br_2	88.95	210.27	238.88	72.79	196.39	226.27
CCl_2Br_2	196.67	261.45	293.61	178.85	244.4	277.34
CH_3F	7.24	15.98	15.98	2.12	12.54	12.54
CH_3Cl	10.45	29.82	29.82	1.96	23.01	23.01
CH_3Br	12.56	39.43	39.43	1.95	30.62	30.62
CF_3H	30.97	30.98	49.19	24.99	24.99	43.52
CF_3Cl	53.09	82.10	83.00	42.96	74.16	74.17
CF_3Br	55.18	120.4	120.41	42.99	110.1	110.11
CCl_3H	90.87	90.88	158.26	76.86	76.87	147.25
CCl_3F	115.05	115.07	158.22	101.43	101.44	146.46
CCl_3Br	162.39	220.74	220.77	145.87	205.26	205.29
CBr_3H	195.93	196.08	361.76	176.56	176.71	347.42
CBr_3F	223.34	248.95	335.5	205.17	231.43	320.23
CBr_3Cl	277.06	277.24	360.16	258.43	258.61	342.86
CH_2FCl	16.41	52.3	56.94	8.04	44.58	50.36
CH_2FBr	18.76	73.54	78.43	8.31	63.92	70.24
CH_2ClBr	25.28	123.78	132.07	11.45	111.41	121.33
CF_2HCl	34.34	60.53	78.61	25.33	52.25	71.04
CF_2HBr	36.55	90.79	108.89	25.5	80.86	99.82
CF_2ClBr	77.76	150.58	170.12	63.47	138.12	158.60
CCl_2HF	48.05	88.1	116.32	36.4	77.14	106.89
CCl_2HBr	93.29	143.16	210.75	77.27	127.58	198.52
CCl_2FBr	118.13	170.36	212.77	102.53	155.59	199.92
CBr_2HF	59.76	192.26	227.76	44.24	177.96	215.71
CBr_2HCl	115.59	193.9	281.51	97.76	176.55	268.16
CBr_2FCl	143.26	219.74	282.81	126.11	203.48	269.01
$C(CH_3)_4$	81.67	81.68	81.69	67.48	67.49	67.49
$C(CF_3)_4$	450.78	450.91	450.98	427.58	427.71	427.78
$C(CCl_3)_4$	1181.72	1181.76	1181.88	1135.56	1135.71	1135.59
$C(CBr_3)_4$	2625.35	2625.55	2625.83	2564.80	2565.01	2565.28

Table 1. (b) The Same as Part **(a)**, but for the (*R*) and (*S*) Enantiomers of the Asymmetric Molecules C{X}[a], C{(CX$_3$)}[b], C{(CXH$_2$)}[c] and C{(CX$_2$H)}[d]

Asymmetric molecule	Diamagnetic χ	Paramagnetic χ	Total
C{X} (*R*)	$\begin{bmatrix} -250.4 & 0.00 & -1.04 \\ 0.00 & -613.9 & -1.38 \\ -1.04 & -1.38 & -759.3 \end{bmatrix}$	$\begin{bmatrix} 185.8 & 0.05 & 0.71 \\ 0.05 & 554.1 & 1.38 \\ 0.71 & 1.38 & 708.0 \end{bmatrix}$	$\begin{bmatrix} -64.67 & 0.05 & -0.33 \\ 0.05 & -59.91 & 0.00 \\ -0.33 & 0.00 & -51.27 \end{bmatrix}$
C{X} (S)	$\begin{bmatrix} -250.4 & 0.00 & 1.04 \\ 0.00 & -613.9 & -1.38 \\ 1.04 & -1.38 & -759.3 \end{bmatrix}$	$\begin{bmatrix} 185.8 & -0.05 & -0.71 \\ -0.05 & 554.1 & 1.38 \\ -0.71 & 1.38 & 708.0 \end{bmatrix}$	$\begin{bmatrix} -64.67 & -0.05 & 0.33 \\ -0.05 & -59.91 & 0.00 \\ 0.33 & 0.00 & -51.27 \end{bmatrix}$
C{(CXH$_2$)} (*R*)	$\begin{bmatrix} -816.6 & 0.40 & 1.97 \\ 0.40 & -1989.7 & -1.6 \\ 1.97 & -1.6 & -2023.2 \end{bmatrix}$	$\begin{bmatrix} 698.1 & 4.70 & -2.40 \\ 4.70 & 1876.9 & 5.49 \\ -2.4 & 5.49 & 1914.5 \end{bmatrix}$	$\begin{bmatrix} -118.6 & 5.1 & -0.42 \\ 5.1 & -112.8 & 3.9 \\ -0.42 & 3.9 & -108.7 \end{bmatrix}$
C{(CXH$_2$)} (S)	$\begin{bmatrix} -816.6 & -0.40 & -1.97 \\ -0.40 & -1989.7 & -1.6 \\ -1.97 & -1.6 & -2023.2 \end{bmatrix}$	$\begin{bmatrix} 698.1 & -4.70 & 2.40 \\ -4.70 & 1876.9 & 5.49 \\ 2.4 & 5.49 & 1914.5 \end{bmatrix}$	$\begin{bmatrix} -118.6 & -5.1 & 0.42 \\ -5.1 & -112.8 & 3.9 \\ 0.42 & 3.9 & -108.7 \end{bmatrix}$
C{(CX$_2$H)} (R)	$\begin{bmatrix} -2066.6 & 0.33 & -3.51 \\ 0.33 & -3362.0 & -0.99 \\ -3.51 & -0.99 & -3546.4 \end{bmatrix}$	$\begin{bmatrix} 1910.8 & -0.81 & 2.47 \\ -0.81 & 3208.5 & -1.90 \\ 2.47 & -1.90 & 3396.2 \end{bmatrix}$	$\begin{bmatrix} -156.0 & -0.52 & -1.09 \\ -0.52 & -153.4 & -2.90 \\ -1.09 & -2.90 & -150.5 \end{bmatrix}$
C{(CX$_2$H)} (S)	$\begin{bmatrix} -2066.6 & -0.33 & 3.51 \\ -0.33 & -3362.0 & -0.99 \\ 3.51 & -0.99 & -3546.4 \end{bmatrix}$	$\begin{bmatrix} 1910.8 & 0.81 & -2.47 \\ 0.81 & 3208.5 & -1.90 \\ -2.47 & -1.90 & 3396.2 \end{bmatrix}$	$\begin{bmatrix} -156.0 & 0.52 & 1.09 \\ 0.52 & -153.4 & -2.90 \\ 1.09 & -2.90 & -150.5 \end{bmatrix}$
C{(CX$_3$)} (*R*)	$\begin{bmatrix} -3465.6 & -1.38 & 1.19 \\ -1.38 & -4560.9 & 0.33 \\ 1.19 & 0.33 & -5154.9 \end{bmatrix}$	$\begin{bmatrix} 3294.5 & 0.43 & 1.57 \\ 0.43 & 4378.9 & -3.23 \\ 1.57 & -3.23 & 1046.2 \end{bmatrix}$	$\begin{bmatrix} -170.9 & -0.94 & 2.77 \\ -0.94 & -181.9 & -2.94 \\ 2.77 & -2.94 & -4108.7 \end{bmatrix}$
C{(CX$_3$)} (S)	$\begin{bmatrix} -3465.6 & 1.38 & -1.19 \\ 1.38 & -4560.9 & 0.33 \\ -1.19 & 0.33 & -5154.9 \end{bmatrix}$	$\begin{bmatrix} 3294.5 & -0.43 & -1.57 \\ -0.43 & 4378.9 & -3.23 \\ -1.57 & -3.23 & 1046.2 \end{bmatrix}$	$\begin{bmatrix} -170.9 & 0.94 & -2.77 \\ 0.94 & -181.9 & -2.94 \\ -2.77 & -2.94 & -4108.7 \end{bmatrix}$

[a]C{X} = CHFClBr. [b]C{(CX$_3$)} = C(CH$_3$)(CF$_3$)(CCl$_3$)(CBr$_3$). [c]C{(CXH$_2$)} = C(CHH$_2$)(CFH$_2$)(CClH$_2$)(CBrH$_2$) [d]C{(CX$_2$H)} = C(CH$_2$H)(CF$_2$H)(CCl$_2$H)(CBr$_2$H).

correlation are studied.

The DFT-B3LYP/6-311G optimized geometric parameters (bond lengths) and the natural bond orbital (NBO) charges on the terminal atoms (q$_a$) and groups (q$_g$) calculated for the **A-E** series of molecules are reported respectively in Tables S1-S5 of the Supplementary Materials. Analysis of the results reported in Tables S1-S4 for the **A-D** series of molecules confirms definite role of the distance of the terminal groups from the chiral center on the atomic and group charges, which can consequently affect the MST elements values. For the **E** series of molecules (Table S5) no clear correlation is observed between atomic/group charges and the branch length. Detailed analysis of the bond lengths and electric charges is presented in Supplementary Materials.

Magnetic susceptibility tensor (MST) and specific optical rotation $[\alpha]_D$ for the **A-E** series of molecules are calculated at DFT-B3LYP/6-311G level of theory using GIAO method. In the first attempt, possible correlation between the individual off-diagonal elements of MST and the calculated optical activity of the **A** family of molecules is studied and visualized in Fig. 2a. This Fig. shows that these two quantities are not correlated. Values of diagonal and off-diagonal elements of MST depend on the number of electrons of the molecule, while optical rotation depends on the extent of the asymmetry of the electron density only. Therefore, in order to establish any correlation between these two quantities, it is necessary to normalize these values with respect to the number of active electrons or some physically relevant function of the number of electrons of the molecule. A number of different normalizations (reductions) are examined to investigate possible correlation with optical rotation, including normalizations with respect to: 1) The total number of electrons n_{tot}, 2) The number of valence electrons, n_v, 3) The isotropic part of the MST, χ_{iso}, 4) The sum of the two corresponding diagonal elements, *e.g.* $(\chi_{qq} + \chi_{q'q'})$ for the off-diagonal element $\chi_{qq'}$, and 5) The anisotropic part of MST, χ_{aniso} ed in Eq. (4). These normalizations are carried out to obtain the normalized (reduced) MST elements $\chi^{i}_{qq'}$ (i = 1-5) from the original MST elements $\chi_{qq'}$ *via*:

$$\chi^{i}_{qq'} = \frac{\chi_{qq'}}{S^{i}}, \qquad q, q' = x, y, z \tag{6}$$

in which S^i is the normalization scale for the i-th case defined above and summarized in Table 2.

The original and normalized (reduced) off-diagonal elements of the MST, χ^{j}; i = 1-4, calculated for the **A** series of molecules are plotted in Fig. 2 against the corresponding calculated optical activities. It can be seen clearly from this figure that there is no correlation between optical activity and the $\chi^{1}_{qq'}$, $\chi^{2}_{qq'}$, $\chi^{3}_{qq'}$ and $\chi^{4}_{qq'}$ normalized off-diagonal elements of MST. This is while, the $\chi^{5}_{qq'}$ reduced MST elements calculated for the **A** series of molecules (plotted in Fig. 3a) show a relatively weak correlation with the calculated optical activities. Existence of such a correlation is examined for other (**B-E)** series of molecules in Figs. 3b to 3e. As is evident from these figures, the reduced quantity $\chi^{5}_{qq'}$ does not show either any well-behaved correlation with optical activity. It is therefore required to carry out normalization with respect to another quantity, which is more closely representative of the contributing electrons in the response of the molecules to the external magnetic field.

Based on the dependence of the diamagnetic susceptibility (the first term in Eq. (3)) on the electronic spatial extent (ESE) $<r^2>$ of molecule, normalization of the off-diagonal elements of MST with respect to ESE, *i.e.* $\chi^{6}_{qq'} = \frac{\chi_{qq'}}{S^{6}}$ with $S^6 = <r^2>$, may result in a quantity correlated to the optical activity. This normalization does not alter asymmetry of the electronic density represented by MST elements. To normalize MST elements in this way, ESE values of the model molecules are calculated using the ground state Slater determinant electronic wavefunction D_0, based on the Kohn-Sham spin-orbitals obtained in the DFT-B3LYP calculations *via* $<r^2> = <D_0|r^2|D_0>$. The $\chi^{6}_{qq'}$ normalized quantities thus obtained are plotted against optical activities in Fig. 4. This Figure shows a very good correlation between the reduced susceptibility $\chi^{6}_{qq'}$ and specific optical rotation $[\alpha]_D$. Almost the same level of correlation is obtained between the optical activity and all ESE-normalized off-diagonal elements of MST (χ^6) for all of the **A-E** series of molecules. It can thus be said that this correlation is general and physically meaningful, and does not depend on the type of the molecule.

Possible effects of the inclusion of unrestricted Slater determinants in the SCF calculations are examined by running geometry optimization and calculation of molecular properties at the UB3LYP level of theory in which the α and β electrons are not forced to have identical orbitals. Results of this study show that only the MST elements of the **C** series of molecules are changed slightly which can be attributed to their extended (coupled) π-systems.

The MST data reported in Table 1b shows that the residual susceptibility is of diamagnetic nature. Therefore,

Table 2. The Normalization Scale for the *i*-th Case Described in the Text, S^i, Used to Obtain the Normalized (Reduced) MST Elements $\chi^i_{qq'}$ from the Original MST Elements $\chi_{qq'}$

I	1	2	3	4	5	6
S^i	n_{tot}	n_v	χ_{iso}	$(\chi_{qq} + \chi_{q'q'})$	χ_{aniso}	$<r^2>$

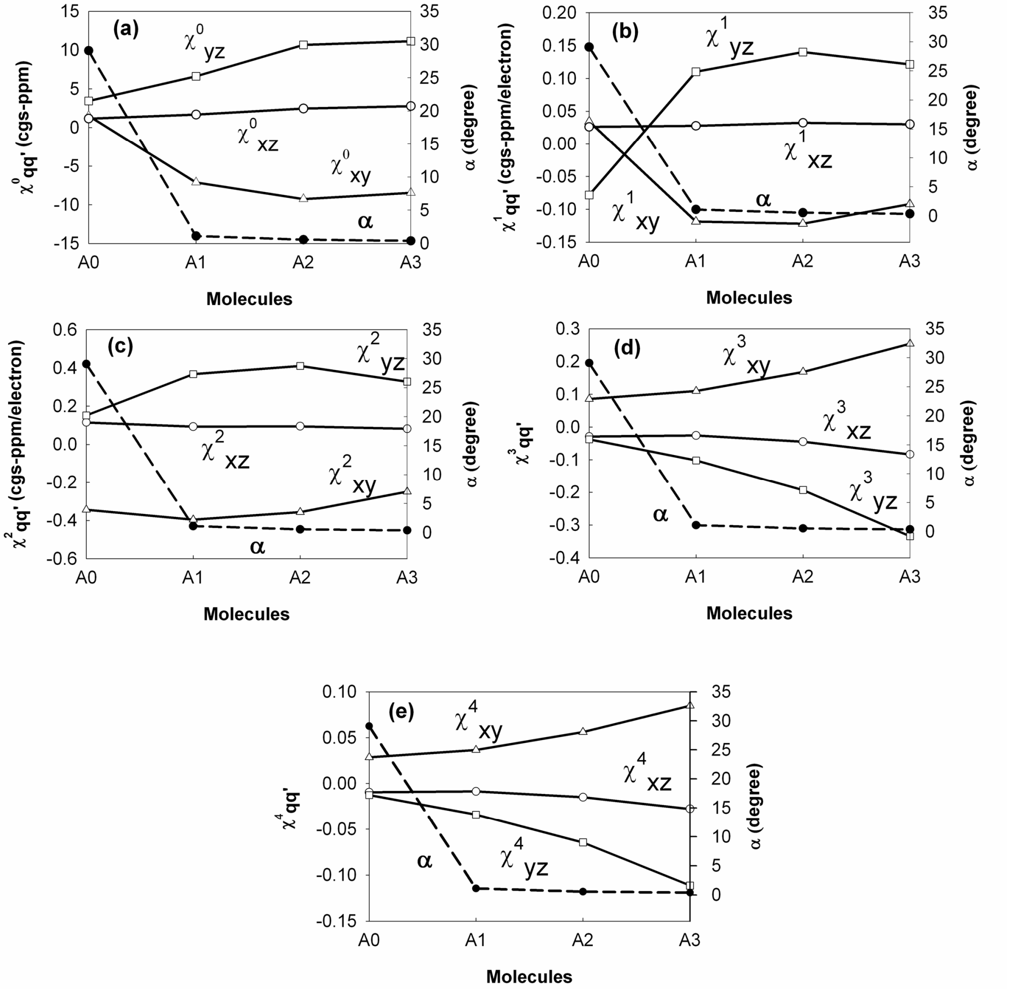

Fig. 2. Correlation between optical activity α and the $\chi^0_{qq'}$ (in cgs-ppm), $\chi^1_{qq'}$, $\chi^2_{qq'}$ (in cgs-ppm/electron), $\chi^3_{qq'}$ and $\chi^4_{qq'}$ (both dimensionless) reduced off-diagonal elements of the magnetic susceptibility tensor (MST) calculated for the **A** series of molecules (introduced in Fig. 1) using Eq. (6).

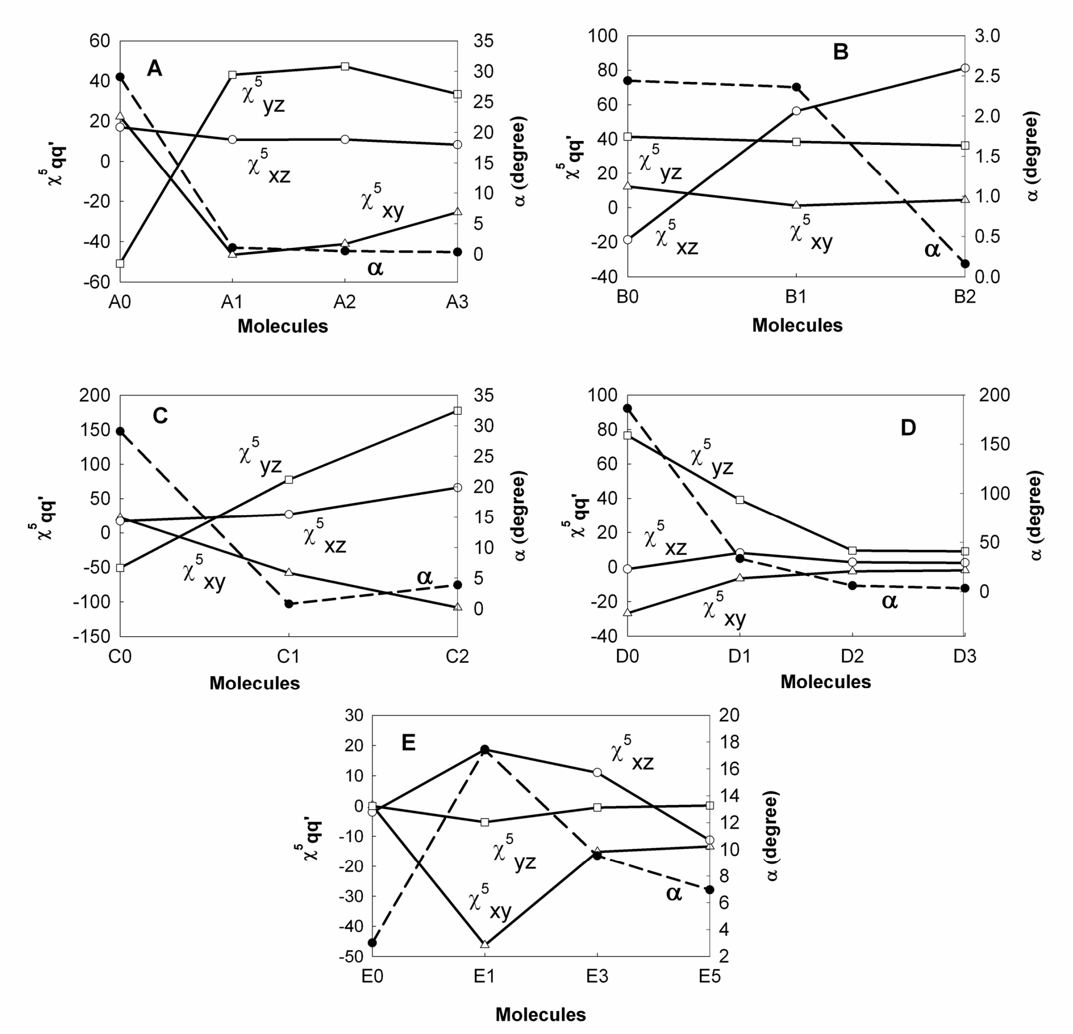

Fig. 3. Correlation between optical activity α and the dimensionless $\chi^5_{qq'}$ reduced off-diagonal elements of the magnetic susceptibility tensor (MST) calculated for the **A**-**E** series of molecules (introduced in Fig. 1) using Eq. (6).

the correlation between the specific optical rotation $[\alpha]_D$ and the $\chi^6_{qq'}$ normalized susceptibility tensor elements reduced by electronic spatial extent $<r^2>$ is justified.

Effects of Substitutions and their Distances from the Chiral Center on Optical Activity

In this section, effects of the type and distance of the substitutions from the chiral center on the optical activity and its correlation with magnetic susceptibility tensor elements are studied. Since, only the $\chi^6_{qq'}$ normalized elements of MST (χ) showed good correlation with the optical rotation $[\alpha]_D$, in the rest of this article, only this quantity will be used for our theoretical study.

To study the effect of the type of substitutions on the optical activity, we need a series of molecules that are different in the electron density of their substitutions but with identical distances (in terms of the number of bonds) from the chiral center. Comparison between the calculated values of optical activities for the corresponding members of the **A** and **B** series of molecules, *i.e.* $\mathbf{A}_n$ with $\mathbf{B}_n$, shows that optical activity is decreased by going from $\mathbf{A}_n$ to $\mathbf{B}_n$ due to the decrease in the electron density of the substitutions.

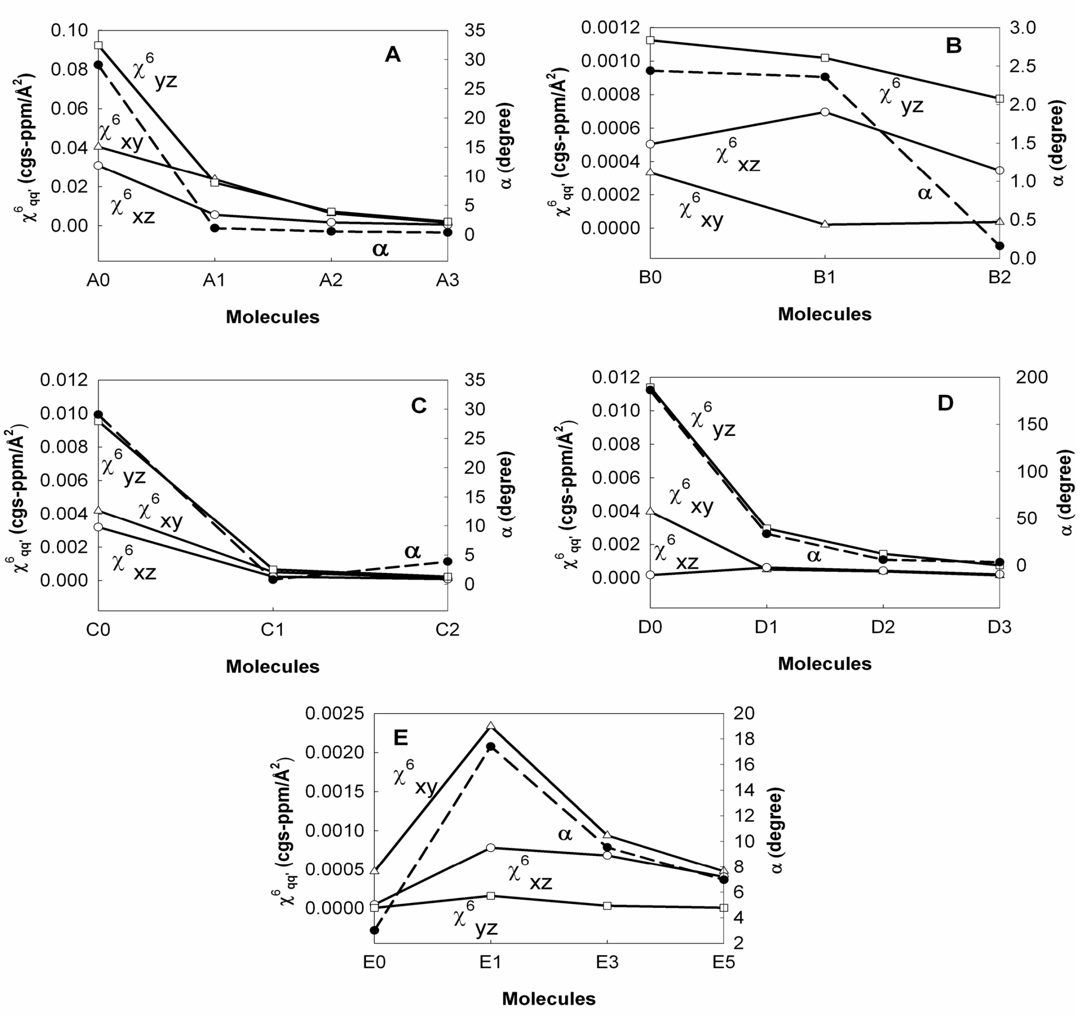

Fig. 4. Correlation between optical activity α and the $\chi^{6}_{qq'}$ (in cgs-ppm/Å^2) reduced off-diagonal elements of the magnetic susceptibility tensor (MST) calculated for the **A-E** series of molecules (introduced in Fig. 1) using Eq. (6), with $S^{(6)} = <r^2> = ESE$.

The same comparison between the corresponding members of the **A** and **D** series of molecules shows that optical activity is increased by going from $\mathbf{A}_n$ to $\mathbf{D}_n$ due to the increase in the electron densities of the substitutions. In comparison to the ending set of atoms (H, Be-H, F and Cl), responsible for electron density asymmetry and optical rotation in the **A** series, the (CH_3, Be-CH_3, CF_3 and CCl_3) set of groups of atoms, responsible for the asymmetry of the electron density in the **B** series, have lower electron density asymmetry. Note that application of the S_n symmetry operations on the **B** series of molecules results in smaller differences in the electron density because of wider spread of the electron density in the **B** series. In other words, the electron density asymmetry in the **B** series is closer to the S_n symmetry and thus causes smaller optical rotation. While, for the **D** series of molecules having (H, Li, Na and K) as the set of ending atoms, due to the lack of non-bonding electrons on these atoms, the electron density asymmetry is much higher, and thus they have higher optical rotation.

The slope of the variation of the calculated optical activity with the distance of the substitutions has the largest value for the **D** series. Since substitutions in this series of molecules have the largest electron densities and the largest differences, distancing the substitution from the chiral center results in the largest decrease in the optical rotation.

Effect of the type of the branch units (atoms or groups), by which distance of the substitution from the chiral center is increased, on the optical activity can be studied by comparing the results obtained for the corresponding members of the **A** and **C** series of molecules, *i.e.* $\mathbf{A}_n$ with $\mathbf{C}_n$. This comparison shows that the molecular series **C** with acetylide (-C≡C-) group as the branch units, have smaller optical activity from their corresponding molecules in the **A** series which have Be atom as its branch unit. This is quite obvious and expected as the substitutions in charge of the electron density asymmetry get distance from the chiral center by the addition of one unit much faster in the **C** series than that in the **A** series.

CONCLUSIONS

Optical activities of the model molecules with one chiral center are correlated to the off-diagonal elements of magnetic susceptibility tensor (MST) reduced with respect to the molecular electronic spatial extent. Present study shows clearly that how optical activity depends on the electron density differences between the terminal groups of the branches, which are responsible for the asymmetry of the electron density around a chiral center. Increasing electron density differences of the substitutions (while keeping their distances from the chiral center constant) results in higher optical activity. Furthermore, optical activity depends strongly on the lengths of the branches such that it is effectively reduced upon distancing the substitutions from the chiral center. Results of this work present a more clear description of the physical basis of the optical rotation.

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