



Vibrational Spectra of 4-hydroxy-3-cyano-7-chloro-quinoline by Density Functional Theory and ab initio Hartree-Fock Calculations

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ABSTRACT

The infrared vibrational spectra of 4-hydroxy-3-cyano-7-chloro-quinoline (4H3CN7CLQ) molecule in the solid phase were download from the NIST Chemistry WebBook. In order to calculate the frequency of molecular vibrations the 4H3CN7CLQ molecule was optimized in the HF and DFT theories in the basic case. All frequencies calculated with HF/6-311G(dp) and DFT/B3LYP/6-311G(dp) were scaled to 0.9085 and 0.9669, respectively. All calculations were not limited and performed on a personal computer using GaussView visualization and GAUSSIAN09 program package. The frequencies values obtained by scaling were compared with the experimental values one by one. Correlation graphs were drawn between experimental and theoretical values. However, some modes of vibration frequencies are also provided. The frequency values obtained from the HF and DFT methods are seen in good agreement with the experimental data.

Keywords: 4-hydroxy-3-cyano-7-chloro-quinoline, IR, HF, DFT

4-hidroksi-3-siyano-7-kloro-kinolin'in Yoğunluk Fonksiyon Teorisi ve Hartre Fock ile titreşim spektrumunun hesaplanması

ÖZ

4 - hidroksi - 3- siyano -7-kloro - kinolin (4H3CN7CLQ) molekülünün katı fazdaki kızılötesi titreşim spektrumu, NIST Chemistry Web sayfasından alındı. Moleküler titreşimlerin frekansını hesaplamak için, temel durumda HF ve DFT teorilerinde 4H3CN7CLQ molekülünün optimize edilmesi yapıldı. HF / 6-311G (dp) ve DFT / B3LYP / 6-311G (dp) ile hesaplanan tüm frekanslar sırasıyla 0.9085 ve 0.9669 ile ölçeklendirildi. Tüm hesaplamalar sınırlandırılmadan GaussView ve GAUSSIAN09 paket programı kullanılarak kişisel bilgisayarda yapıldı. Ölçekleme ile elde edilen frekans değerleri, deneysel değerlerle bire bir karşılaştırıldı. Deneysel ve teorik veriler arasında korelasyon grafikleri çizildi. Bununla birlikte bazı titreşim frekanslarının şekilleri verilmiştir. HF ve DFT yöntemlerinden elde edilen frekans değerlerinin deney verileri ile iyi uyum içinde olduğu görülmektedir.

Anahtar Kelimeler: 4-hidroksi-3-siyano-7-kloro-kinolin, IR, HF, DFT

1. INTRODUCTION

8-Hydroxyquinoline and its derivatives are well known with their antibacterial, antifungal and antiamoebic activities.¹ Quinoline derivatives have attracted a special interest due to their therapeutic properties.² Quinoline sulphonamides have been used in the treatment of tuberculosis, malaria, diabetes and cancer.³⁻⁶ Recently, Arjunan and co-workers⁷ have calculated the infrared vibrations of the 7-bromo-5-chloro-8-hydroxyquinoline molecule by the HF and DFT methods. Arıcı and Yılmaz⁸ have studied infrared spectrum of 2-Methyl-8-quinolinol using DFT and HF theoretical calculations. At present, there is no theoretical infrared vibrational work on the 4-hydroxy-3-cyano-7-chloro-quinoline molecule in the literature. In this study,

vibrational frequency results of 4-hydroxy-3-cyano-7-chloro-quinoline molecule are obtained by ab initio HF and DFT calculations. Optimal vibrational wavenumbers and modes of 4-hydroxy-3-cyano-7-chloro-quinoline molecule are also given.

2. EXPERIMENTAL

In this study, 4-hydroxy-3-cyano-7-chloro-quinoline molecule is named as 4H3CN7CLQ. Infrared spectra of 4H3CN7CLQ recorded between 4000-600 cm⁻¹ using solid KBR pellet of 1.0% were download from the NIST Chemistry WebBook.⁹ Infrared spectra of 4H3CN7CLQ recorded between 4000-600 cm⁻¹ using solid KBR pellet of 1.0%.

2.1. Computational details

The 4H3CN7CLQ was optimized in the base case using the 6-311G(dp) baseline set in HF and DFT/B3LYP method. The optimized parameters were used in the vibrational frequency calculations at HF and DFT levels. DFT for all studies reported in this paper was calculated from Eq. (1)

$$E_{xc} = (1 - a_0) E_x^{LSDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} + a_c E_c^{LYP} + (1 - a_c) E_c^{VWN} \quad (1)$$

Where, the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke's exchange functional correlation, the gradient correlated functional correlation of Lee, Yang and Parr and the local correlation functional of Vosko, Wilk and Nusair¹⁰, respectively.

HF/6-311G(dp) and DFT/B3LYP/6-311G(dp) levels of theory with the optimized geometries were used to calculate infrared vibrations of the 4H3CN7CLQ molecule. All the calculated vibrational frequencies was scaled by 0.9085 for HF/6-311G(dp) and 0.9669 for BLYP/6-311G(dp).¹¹ All calculations were made on a computer using GaussView¹² visualization and GAUSSIAN09¹³ package programs without limitation of the molecular structure.

3. RESULTS AND DISCUSSION

The 4H3CN7CLQ molecule includes 19 atoms. The 51 normal vibrational modes are distributed in the a' and a'' symmetry species at the Cs point group. The normal vibrations of a' and a'' can be attributed to the plane-in and plane-out modes, respectively. All vibrations are both infrared and Raman active. The molecular structure of the 4H3CN7CLQ and numbering of atoms in the molecule are shown in Figure 1.

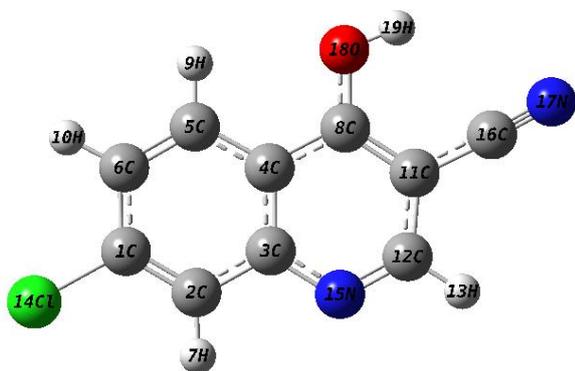


Figure 1. The molecular structure of 4H₃CN₇CLQ.

3.1. Vibrational Assignments

The observed infrared spectra of the 4H3CN7CLQ molecule are given in Figure 2. The frequencies calculated with HF/6-311G(dp) and DFT/B3LYP/6-

311G(dp) are given in Table 1 with their relative intensities, probable assignments. The observed frequencies are usually lower than the corresponding calculated frequencies which are unscaled. It is well known that HF method tends to overestimate vibrational frequencies.

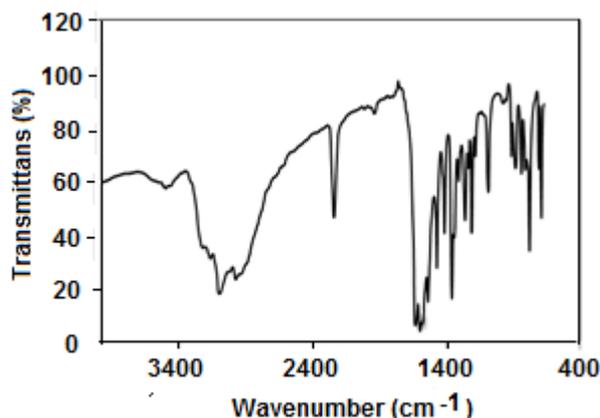


Figure 1. Infrared spectra of 4H₃CN₇CLQ molecule.

3.1.1. O-H vibrations

O-H vibrations are sensitive in hydrogen-bonded molecules, so marking them is difficult. The non-hydrogen bonded or free hydroxyl group give a strong absorption peak in 3700-3500 cm⁻¹.¹⁴ For solids, liquids and concentrated solutions, a broad band of less intensity is observed normally. If Inter-molecular hydrogen bonding is present, the O-H stretching band would reduce to 3550-3200 cm⁻¹ region.¹⁵ The computed wave number for the O-H stretching is observed at 3737.950 cm⁻¹ by HF/6-311G(d,p) and at 3738.723 cm⁻¹ by B3LYP/6-311G(d,p), while the O-H stretching in the experimental FT-IR spectrum are observed at 3500 cm⁻¹. The O-H in-plane bending vibrations are mixed with C-H stretching vibrations. In-plane O-H vibrations were observed between 1440- 1260 cm⁻¹.¹⁶ The experimentally observed strong band at 1216 cm⁻¹ can be assigned to O-H in-plane bending vibration. This band is calculated at 1229.872 cm⁻¹ by HF/6-311G(d,p) and at 1259.441 cm⁻¹ by B3LYP/6-311G(d,p) method. The O-H out-of-plane bending vibrations are appeared as broad region around 700-600 cm⁻¹. The strong band observed at 696 cm⁻¹ at the spectrum is assigned to O-H out-of-plane bending vibration, which shows good correlation with computed wave number at 689.094 cm⁻¹ by HF/6-311G(d,p) and at 682 cm⁻¹ by B3LYP/6-311G(d,p) methods. The weak band observed at 1187 cm⁻¹ indicates C-(OH) stretching band, whereas this band have been calculated at 1176.953 cm⁻¹ by the HF/6-311G(d,p) and at 1204,272 cm⁻¹ by the B3LYP/6-311G(d,p), respectively. Some researchers have assigned C-(OH) stretching band around 1200 cm⁻¹ in substituted benzenes and pyridine molecule.^{17,18}

Table 1. The observed infrared wavenumbers and calculated frequencies using HF/6-311G(dp) and DFT/B3LYP/6-311G(dp) with scaled frequencies, their intensities and probable assignments of 4H3CN7CLQ

N.	S.	Calculation HF/6-311G(dp)			Calculation BLYP/6-311G(dp)			Exp. (cm ⁻¹) ¹	Approximate description
		Unscaled (cm ⁻¹)	Scaled ^a (cm ⁻¹)	Infrared int.	Unscaled (cm ⁻¹)	Scaled ^b (cm ⁻¹)	Infrared int.		
1	A''	63.002	57.237	1.3831	57.683	57.504	1.130	-----	Butterfly
2	A''	127.209	115.569	0.3266	115.038	114.682	0.222	-----	Torsion Molecule
3	A'	130.715	118.754	7.314	115.685	115.326	6.397	-----	δ (C≡N)
4	A''	184.443	167.567	4.981	168.317	167.796	4.225	-----	δ Molecule
5	A'	223.296	202.865	2.761	204.513	203.879	2.170	-----	δ (C-Cl) + δ (C-OH)
6	A''	286.651	260.422	0.141	260.572	259.764	0.420	-----	γ (CCC)
7	A''	311.493	282.991	6.602	285.172	284.288	4.966	-----	Fluctation
8	A'	312.847	284.221	2.609	291.1792	290.276	2.415	-----	γ (CCC)
9	A'	391.502	355.679	6.158	364.865	363.734	6.243	-----	γ (CCC)
10	A''	468.565	425.692	98.163	437.168	435.813	26.070	-----	δ (C-OH)
11	A''	493.862	448.674	32.485	468.122	466.671	4.460	-----	δ (CCC)+δ (CCN)
12	A'	504.858	458.663	8.093	474.876	473.404	5.130	-----	γ (CCC)
13	A'	512.480	465.588	1.901	491.4503	489.926	50.563	-----	γ (CCC)
14	A''	540.161	490.736	1.301	492.732	491.205	32.424	-----	δ (CCC)
15	A'	577.716	524.854	2.620	537.518	535.851	3.538	-----	γ (CCC)
16	A'	613.981	557.802	3.273	571.347	569.575	0.499	-----	δ (CCC)
17	A''	629.762	572.138	0.353	571.886	570.113	3.311	-----	δ (CCC)
18	A'	684.579	621.940	0.039	638.569	636.590	0.319	-----	δ (CCN)
19	A''	709.142	644.255	7.207	645.7285	643.726	5.735	-----	γ (CCC) + γ (CNC)
20	A'	758.497	689.094	0.992	699.731	697.562	14.253	696 s.	δ (CCC)
21	A''	773.134	702.392	19.713	706.668	704.477	2.1463	712 m.	γ (O-H)
22	A'	847.389	769.853	26.409	790.111	787.662	30.424	784 s.	ν(C-Cl)
23	A''	882.412	801.671	36.475	798.921	796.444	18.614	814 m.	γ(C-H)
24	A''	932.683	847.342	7.628	846.018	843.395	12.495	841 m.	γ(C-H)
25	A'	988.191	897.771	61.037	913.982	911.149	11.541	888 m.	δ (CCC)
26	A''	1009.357	917.000	21.848	915.393	912.555	54.068	918 w.	γ(C-H)
27	A'	1011.930	919.338	75.725	950.847	947.899	71.132	-----	δ (CCC)
28	A''	1086.895	987.444	4.181	960.247	957.270	8.192	979 w.	γ(C-H)
29	A''	1107.031	1005.737	0.751	988.649	985.585	0.887	-----	γ(C-H)
30	A'	1152.299	1046.864	38.854	1083.254	1079.896	40.163	1089 m.	Ring Breathing
31	A'	1186.092	1077.564	30.358	1137.942	1134.414	14.115	-----	δ(C-H)
32	A'	1232.556	1119.777	42.117	1195.758	1192.051	46.715	1187 w.	ν(C-OH)
33	A'	1295.490	1176.953	6.560	1208.019	1204.274	5.290	-----	δ(C-H)
34	A'	1353.739	1229.872	65.053	1263.357	1259.441	70.196	1216 s.	δ(O-H)
35	A'	1378.370	1252.249	3.727	1280.163	1276.195	8.644	1265 s.	δ(C-H)
36	A'	1399.001	1270.992	29.103	1292.227	1288.221	31.244	1312 m.	δ(C-H)
37	A'	1433.059	1301.934	54.790	1358.340	1354.129	38.757	1345 s.	Ring ν(C-C)
38	A'	1483.143	134.435	45.820	1385.083	1380.790	49.139	1364 v.s.	Ring ν(C-C)
39	A'	1533.148	1392.865	65.705	1421.695	1417.287	44.677	1420 s.	Ring ν(C-C)
40	A'	1578.032	1433.642	80.289	1466.028	1461.483	54.311	1447 s.	Ring ν(C-C)
41	A'	1600.953	1454.466	2.264	1476.435	1471.858	1.2246	-----	Ring ν(C-C)
42	A'	1638.573	1488.644	102.302	1516.220	1511.520	86.740	1541 v.s.	Ring ν(C-C)
43	A'	1757.813	1596.973	202.014	1592.599	1587.662	133.577	1585 v.s.	Ring ν(C-C) + ν(C-N)
44	A'	1796.870	1632.457	24.111	1634.487	1629.420	9.1501	1602 v.s.	Ring ν(C=C)
45	A'	1823.409	1656.567	388.168	1651.032	1645.914	235.855	1636 v.s.	Ring ν(C=C)+ ν(C=N)
46	A'	2569.205	2334.122	105.272	2318.738	2311.549	78.652	2243 s.	ν(C≡N)
47	A'	3328.739	3024.159	10.885	3154.583	3144.804	7.607	2979 s. br	ν(C-H)
48	A'	3364.817	3056.936	0.239	3199.817	3189.898	0.080	3102 s. br	ν(C-H)
49	A'	3382.392	3072.903	1.568	3213.726	3203.763	1.022	3168 s.br.	ν(C-H)
50	A'	3385.895	3076.085	0.928	3219.655	3209.674	0.846	3225 s.br.	ν(C-H)
51	A'	4114.420	3737.950	166.759	3750.349	3738.723	112.306	3500 br.	ν(O-H)

^aScaling factor (s.f.): 0.9085, ^b(s.f.): 0.9669, def.: deformation, int.: intensity, br.: broad, m.: medium, s.: strong, w.: weak, v.: very, ν: stretching, δ: in-plane bending, γ: out of plane bending, Exp.: Experimental, N.: number, S.: species, W.num.: wavenumber.

3.1.2. C-H vibrations

Usually, CH stretching vibrations in aromatic structures have observed in the region $3000\text{--}3250\text{ cm}^{-1}$ ¹⁹ and they are pure vibrations. In the present study, the bands at 3225 , 3168 , 3102 and 2979 cm^{-1} in infrared spectrum are assigned to C-H stretching vibration (see Table 1). These bands were calculated to be at 3076.085 , 3072.903 , 3056.936 and 3024.159 cm^{-1} by HF/6-31G(d,p) and at 3209.674 , 3203.763 , 3189.898 and 3144.804 cm^{-1} by DFT/B3LYP/6-31G(d,p), respectively. The calculated frequencies in the HF/6-31G(d,p) are shifted down too much, while the frequencies calculated in the DFT/B3LYP/6-31G(d,p) are shifting down less. These assigned frequencies are affected much by the substitutions. The C-H in-plane and out-of-plane bending vibrations generally lies in the ranges $1000\text{--}1300\text{ cm}^{-1}$ and $950\text{--}800\text{ cm}^{-1}$ ²⁰⁻²², respectively. The bands at 1312 , 1265 and 1187 cm^{-1} in infrared spectrum are assigned to C-H in-plane bending vibration, which are calculated at 1270.992 , 1252.249 and 1119 cm^{-1} by HF/6-31G(d,p) and at 1288.221 , 1276.195 and 1192.051 cm^{-1} by DFT/B3LYP/6-31G(d,p), respectively. Three C-H out-of-plane bending vibrations are observed at 1089 , 979 and 918 cm^{-1} . These bands have been calculated to be at 1046.864 , 987.44 and 917.000 cm^{-1} by HF/6-31G(d,p) and 1079.896 , 957.270 and 912.555 cm^{-1} by DFT/B3LYP/6-31G(d,p), respectively. According to the literature, the in-plane and out-of-plane bending vibrational frequencies are found to be within their characteristic regions.

3.1.3. C-Cl vibrations

The C-Cl stretching vibrations give generally a broad band at region $800\text{--}600\text{ cm}^{-1}$ depending on the configuration, conformation and substitutions of compound.²³ A strong infrared spectra band at 784 cm^{-1} is assigned to C-Cl stretching vibration, which is calculated at 796.853 cm^{-1} by HF/6-31G(d,p) and 787.662 cm^{-1} by DFT/B3LYP/6-31G(d,p), respectively. The computed values are well correlated with the experimental observations.

3.1.4. C≡N vibrations

Nitriles are characterized by the C≡N stretching vibrations which occur at $2260\text{--}2240\text{ cm}^{-1}$ in aliphatic nitriles. Conjugation lowers the nitrile frequency, due to resonance, to $2235\text{--}2215\text{ cm}^{-1}$ in most cases.²⁴ The experimentally observed strong band at 2243 cm^{-1} is assigned to C≡N stretching vibration. This band is calculated at 2334.122 cm^{-1} by HF/6-311G(d,p) and at 2311.549 cm^{-1} by B3LYP/6-311G(d,p), respectively. It can be said that the experimentally observed band is greater than calculated theoretically. The reason for this may be attributed to the calculations done in the gas phase.

3.1.5. Skeletal vibrations

The identification of C-N stretching band is a very difficult, since this band is always mixed with other bands. This band is generally observed in the region $1645\text{--}1575\text{ cm}^{-1}$ ²⁵ at pyridine derivatives. C-N stretching vibrations bands in combination with C-C are observed in strong intensity at 1636 and 1585 cm^{-1} . This bands are calculated at 1656.567 and 1659.4973 cm^{-1} by HF/6-31G(d,p) and at 1645.914 and 1587.662 cm^{-1} by DFT/B3LYP/6-31G(d,p), respectively.

In general, the bands which appear between 1430 and 1650 cm^{-1} are C-C stretching vibrations.^{16,18} The C=C stretching vibrations are observed in very strong intensity at 1636 and 1602 cm^{-1} . This bands are calculated at 1657.567 and 1632.457 cm^{-1} by HF/6-31G(d,p) and 1645.914 and 1629.420 cm^{-1} by DFT/B3LYP/6-31G(d,p), respectively. The stretching vibrations bands for C-C bond are obtained in strong intensity at 1585 , 1541 , 1447 , 1420 , 1364 and 1345 cm^{-1} . The experimentally observed these strong bands are found to be in agreement with the theoretically calculated both the intensity and the spectrum bands. The peaks are observed at 888 and 696 cm^{-1} due to C-C-C in-plane bending vibrations.

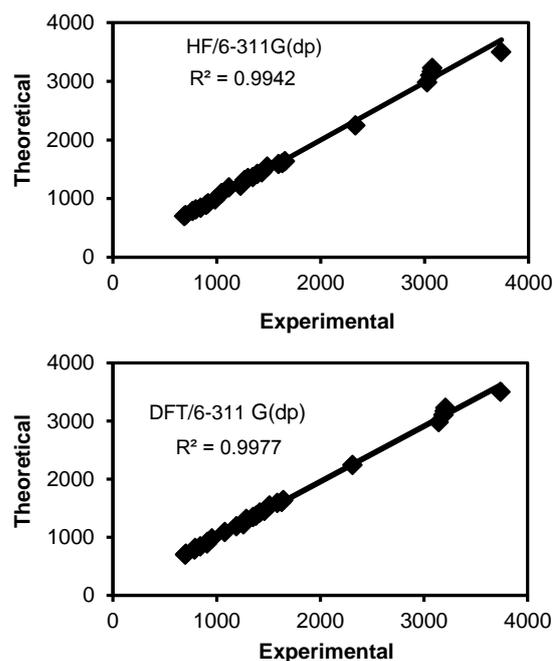


Figure 3. Correlations graphics of frequencies for of 4H3CN7CLQ molecule.

For the 4H3CN7CLQ molecule, the correlation graphs obtained by comparing the frequencies experimentally and theoretically are shown in Figure 3. As can be seen from Figure 3, the experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for DFT/B3LYP than HF for the 4H3CN7CLQ molecule. The some sensitive modes characterized at DFT/B3LYP/6-311G(dp) level in the 4H3CN7CLQ molecule are illustrated in Figure 4.

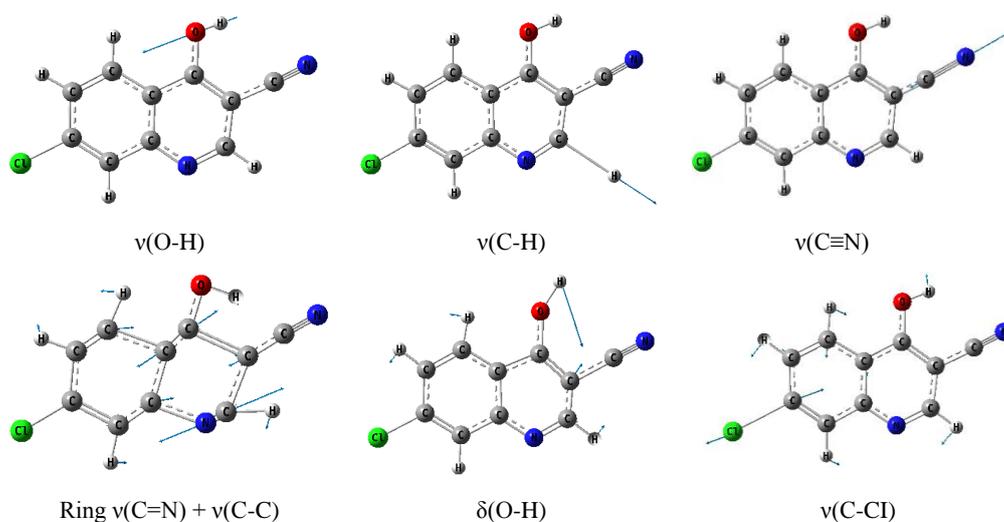


Figure 4. The some sensitive modes characterized at DFT/B3LYP/6-311G(dp) level in 4H3CN7CLQ molecule.

4. CONCLUSION

For the first time, the infrared spectrum of the 4-hydroxy-3-cyano-7-chloro-quinoline molecule was studied theoretically and experimentally. The title compound was theoretically optimized using HF and B3LYP/DFT methods with 6-311G(dp) basis set and calculated the vibrational frequencies. The computed vibrational wavenumbers were assigned and compared with experimental infrared spectra. The infrared absorption and intensities computed by HF and B3LYP methods with 6-311G(dp) basis set were in reasonable agreement with the experimental data. Comparison of the observed fundamental vibrational frequencies and calculated results for this molecule indicates that is superior to scaled HF and B3LYP approach for molecular vibrational problems.

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Conflict of interest

I declare that there is no a conflict of interest with any person, institute, company, etc.

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