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Research Article

Natural bond orbital (NBO) population analysis and non-linear optical (NLO) properties of 2-(azepan-1-yl(naphthalen-1-yl)methyl)phenol

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ABSTRACT

All electronic properties of 2-(Azepan-1-yl (naphthalen-1-yl) methyl) phenol compound were investigated using the density functional theory (DFT) B3LYP method and 6-311 G(d, p) set. Natural bond orbital (NBO) analysis was used to learn the intermolecular and intermolecular binding interaction. Electron distribution was determined by natural population analysis. Nonlinear optical properties (dipole moment μ, polarizability α, and hyperpolarizability β) were investigated to determine the optical properties of the compound. Also, the effect of temperature on thermodynamic parameters (capacity, molar entropy, enthalpy) was reported.

Keywords: NBO, NLO, alkylaminophenol, DFT.

2- (Azepan-1-il (naftalen-1-il) metil) fenolün doğal bağ orbital (NBO) popülasyon analizi ve doğrusal olmayan optik (NLO) özellikleri

ÖZ

2-(Azepan-1-il (naftalin-1-il) metil) fenol bileşiğinin tüm elektronik özellikleri yoğunluk fonksiyonel teori (DFT) B3LYP yöntemi ve 6-311 G (d, p) seti kullanılarak araştırıldı. Moleküller arası ve moleküller arası bağlanma etkileşimini öğrenmek için doğal bağ orbital (NBO) analizi kullanıldı. Elektron dağılımı doğal popülasyon analizi ile belirlendi. Bileşiğin optik özelliklerini belirlemek için doğrusal olmayan optik özellikler (dipol moment μ, polarizabilite α, ve hiperpolarizabilite β)) incelendi. Ayrıca, sıcaklığın termodinamik parametreler (kapasite, molar entropi, entalpi) üzerindeki etkisi rapor edildi.

Anahtar Kelimeler: NBO, NLO, alkilaminofenol, DFT.

1. INTRODUCTION

Alkylaminophenol compounds form a class of heterocyclic compounds used in various fields from pharmacology to polymer chemistry.[1–6] Generally, they are used as drug active material. Also, the phenolic groups have enabled them to have antioxidant activities too. Usually, they are used in chemotherapy for bone cancer treatment. These compounds are obtained generally by the petasis reaction. The reaction takes place by the removal of boric acid from the boronate complex formed by the boronic acid added to the medium after the amine and carbonyl compounds form iminium ion. The fact that the reaction conditions have mild provides it has been preferred in many applications. Although there are many publications on synthesized alkylaminophenols, there are limited studies on its natural bond orbital (NBO), non-linear optical (NLO) and other physical properties. It has been observed in the literature that these compounds are not used outside of medical applications. Besides NBO, NLO is the most useful concept area because of their importance in optoelectronic applications. According to the literature survey, in an earlier study, 2-(Azepan-1-yl(naphthalen-1-yl)methyl)phenol compound which is an alkylaminophenol compound has been synthesized and calculated some of its properties.[7]

However, no any stduy has been reported on the NBO and NLO properties of 2-(Azepan-1-yl(naphthalen-1-yl)methyl)phenol compound so far. Therfore, this study has aimed to determine a NBO analysis of 2-(azepan-1-yl(naphthalen-1-yl)methyl) phenol compound using high-level theoretical methods. Herein, thermodynamic

parameters, standard molar heat capacity, standard molar enthalpy and standard molar entropy have been examined at different temperatures. Moreover NLO

parameters (linear polarizability, anisotropic polarizability and hyperpolarizability) have also been studied using the same method.

2. MATERIALS AND METHODS

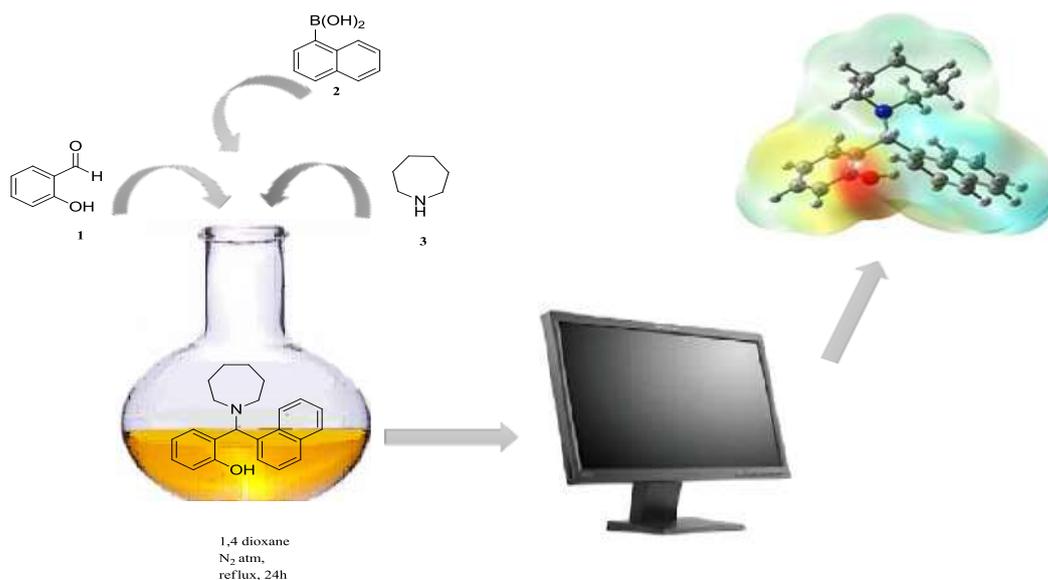### 2.1. Experimental and calculation methods

Figure 1. Synthesis and molecular elektrostatic surface of 2-(Azepan-1-yl(naphthalen-1-yl)methyl)phenol.[7]

2-(Azepan-1-yl(naphthalen-1-yl)methyl)phenol compound was synthesized with petasis reaction. This reaction is a three-component reaction that takes place between aldehyde, amine and boronic acid and used in the previous study.[7] After the experimental characterization of structural, some properties of the compound was determined using theoretical methods. Calculations include the B3LYP theory and 6-311 ++ G (d,p) set which is composed of Becke's three-parameter energy-functional hybrid approac and Lee-Yang and Parr's correlation function[8] in the Gaussian 09W program. Gauss-View 5.0 program was used for molecular modelling.[9]

3. RESULTS AND DISCUSSION

3.1. Natural population analysis

NBO analysis provides all orbital information about electronic density and explains intra-and intermolecular interactions.[10] Also, it gives us an idea of the electron

distributions in the lower shells of atomic orbitals. The distributions of electrons in the shells of atoms is as indicated in Table 1.

Considering Table 1, the highest electronegative charge is observed that is on the atoms of O11 and N33 with the values of -0.69040e and - 0.57169e, and the highest electropositive charge is on H12 and C2 atoms with the values of 0.48133e and 0.31362e, Core: 49.97867 (99.9573% of 50), Valence: 127.39280 (99.5256% of 128), Rydberg: 0.61931 (0.3479% of 178).

3.2. Natural bond orbital (NBO) analysis

NBO analysis gives detailed information about the electron density of all orbitals of the molecule. This information is valuable in that it determines the most accurate Lewis structure for the compound, as well as explains both intermolecular and intermolecular interactions.[11–18] In this study; in the NBO analysis, a second-order Fock matrix was used to evaluate donor-acceptor interactions.[19]

Table 1. Natural charges and distribution of electrons to orbitals for selected atoms in the alkylaminophenol compound

Atom No	Natural Charge	Natural population (e)			
		Core	**Valence**	**Rydberg**	**Total (e)**
C1	-0.23941	1.99905	4.22253	0.01782	6.23941
C2	0.31362	1.99864	3.66366	0.02407	5.68638
C3	-0.09462	1.99889	4.07011	0.02562	6.09462
H8	0.21732	0	0.77935	0.00333	0.78268
H7	0.21603	0	0.78213	0.00184	0.78397
O11	-0.69040	1.99975	6.67768	0.01296	8.69040
H12	0.48133	0	0.51399	0.00467	0.51867
C34	0.08434	1.99903	3.88651	0.03012	5.91566
C35	0.03428	1.99901	3.93808	0.02863	5.96572
C36	-0.22711	1.99914	4.19483	0.03314	6.22711
C38	-0.10426	1.99909	4.07030	0.03487	6.10426
H42	0.20465	0	0.79129	0.00405	0.79535
H40	0.21538	0	0.78065	0.00397	0.78462
C13	-0.07347	1.99909	4.02393	0.05045	6.07347
H14	0.18465	0	0.81060	0.00475	0.81535
N33	-0.57169	1.99944	5.54474	0.02751	7.57169
C15	-0.16835	1.99920	4.14972	0.01943	6.16835
C16	-0.17097	1.99922	4.15126	0.02048	6.17097
H19	0.20578	0	0.79213	0.00209	0.79422
H22	0.20035	0	0.79751	0.00213	0.79965

The second-order Fock-matrix was carried out to evaluate the donor-acceptor interactions within the NBO basis. The interactions result in a lack of occupancy from the localized NBO of the idealized Lewis shape into an empty non-Lewis orbital. For every donor (i) and acceptor (j) the stabilization energy (E2) associated with the delocalization i → j is decided by the subsequent equation:

$$E(2) = \Delta E_{i,j} = q_i [F_{(i,j)}^2] / [E_i - E_j] \qquad (1)$$

Looking at Table 2, it is seen that s-type and p-type subshells contribute to all orbitals. p-type subshell was contributed to C2-C3 antibonding orbital. Also, p-type subshell was contributed to LP N33 orbital, s and p sub-shell was contributed to LP O11 orbital too. When the occupancy values are examined, it is seen that sp hybridization is dominant in the binding orbitals for the compound.

Table 2. Natural atomic orbital occupancies of most interacting NBOs of alkylaminophenol compound along with their percentage of some selected hybrid atomic orbitals

Bonds	Occupancies (e)	Hybrids	AO (%)
σN33-C13	1.97937	$sp^{3.27}$	s(23.4%) p(76.5%) d(0.10%)
σ C13-H14	1.97170	$sp^{3.44}$	s(22.52%) p(77.4%) d(0.08%)
σC2-O11	1.99352	$sp^{3.15}$	s(24.03%) p(75.74%) d(0.22%)
σ O11-H12	1.98303	$sp^{3.52}$	s(22.09%) p(77.81%) d(0.09%)
σC3-C13	1.96326	$sp^{2.20}$	s(31.2%) p(68.77%) d(0.04%)
σC2-C3	1.97340	$sp^{1.59}$	s(38.54%) p(61.42%) d(0.04%)
σC13-C34	1.95385	$sp^{2.66}$	s(27.31%) p(72.65%) d(0.04%)
σC34-C35	1.94128	$sp^{1.87}$	s(34.77%) p(65.15%) d(0.08%)
σN33-C15	1.98281	$sp^{3.20}$	s(23.8%) p(76.07%) d(0.13%)
LP N33	1.86844	$sp^{11.2}$	s(8.32%) p(91.66%) d(0.02%)
LP O11	1.97721	$sp^{1.39}$	s(41.84%) p(58.12%) d(0.03%)
σ*N33-C13	0.03966	$sp^{3.27}$	s(23.4%) p(76.5%) d(0.10%)
σ*C13-H14	0.03932	$sp^{3.44}$	s(22.52%) p(77.4%) d(0.08%)
σ*C2-O11	0.02418	$sp^{3.15}$	s(24.03%) p(75.74%) d(0.22%)
σ*O11-H12	0.01053	$sp^{3.52}$	s(22.09%) p(77.81%) d(0.09%)
σ*C3-C13	0.03650	$sp^{2.20}$	s(31.20%) p(68.77%) d(0.04%)
σ*C2-C3	0.39261	$sp^{1.0}$	s(0%) p(99.95%) d(0.04%)
σ*C13-C34	0.02957	$sp^{2.66}$	s(27.31%) p(72.65%) d(0.04%)
σ*C34-C35	0.02433	$sp^{1.87}$	s(34.77%) p(65.15%) d(0.08%)
σ*N33-C15	0.02661	$sp^{3.20}$	s(23.8%) p(76.07%) d(0.13%)

In NBO analysis, the large *E(2)* value indicates the intense interaction between electron donors and receptors. The O11-H12 bond in the phenyl ring has been found to interact strongly with the naphthalene ring and heterocyclic structure. As seen in Table 3, the molecule; the O11-H12 donor has the highest energy value with 486.90 kcal mol^{-1} where C41-C46 is the acceptor, the O11 donor has the lowest value for the C1-C2 acceptor with 0.51 kcal mol^{-1}.

3.3 Non-linear optical (NLO) analysis

Nonlinear optical (NLO) properties of materials plays

an important role in the design of electronic structure. NLO properties of a compound are originated from π electrons. Increased conjugation or inclusion of donor groups changes NLO properties. In general, quantum chemical calculations explain the relationship between the electronic structure and NLO properties.[16,20–24] One of the compounds used for investigation of NLO properties of molecular systems is p-nitroaniline, thus p-nitroaniline was chosen for the reference compound ın this work. NLO properties of alkylaminophenol compounds have never been studied in the literature before.

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Table 3. Second-order perturbation theory analysis of Fock matrix in NBO basis for selected chemical bonds

NBO(i) (Donor Lewis)	NBO(j) (Acceptor non Lewis)	E(2) kcal mol^{-1}	E(j)-E(i) a.u	F(i,j) a.u	NBO(i) (Donor Lewis)	NBO(j) (Acceptor non Lewis)	E(2) kcal mol^{-1}	E(j)-E(i) a.u	F(i,j) a.u
σC2– O11	σ*C1-C2	0.57	1.48	0.026	σO11-H12	σ*C35-C37	8.30	1.11	0.086
	σ*C1-C6	1.31	1.59	0.041		σ*C41-C46	486.90	0.12	0.216
	σ*C2-C3	1.02	1.49	0.035	σC13-C34	σ*C2-C3	1.62	1.30	0.041
	σ*C3-C4	1.55	1.48	0.043		σ*C3-C13	0.53	1.10	0.022
σC3-C13	σ*C1-C2	2.31	1.19	0.047		σ*C13-C34	0.55	1.02	0.021
	σ*C2-C3	1.50	1.20	0.038		σ*C16-C21	0.58	0.79	0.019
	σ*C4-C5	2.42	1.20	0.048		σ*C16-N33	0.59	1.04	0.022
	σ*C13-N33	0.71	0.82	0.022		σ*C34-C36	0.79	0.67	0.022
	σ*C34-C36	1.82	0.58	0.031		σ*C41-C46	1.93	0.04	0.008
σO11-H12	σ*C1-C2	1.57	1.36	0.041	nO11	σ*C1-C2	0.51	1.16	0.022
	σ*C13-N33	9.40	0.99	0.087		σ*C2-C3	6.12	1.18	0.076
	σ*C13-C34	3.77	1.10	0.058		σ*C2-C3	18.32	0.43	0.086
	σ*C15-H19	4.14	1.50	0.070	nN33	σ*C3-C13	2.67	0.65	0.038
	σ*C16-N33	1.25	1.12	0.033		σ*C15-H19	1.25	0.97	0.032
	σ*C16-H21	18.21	0.86	0.120		σ*C16-C20	9.81	0.58	0.069
	σ*C20-H28	10.94	0.98	0.092		σ*C16-H21	2.00	0.33	0.024
	σ*C23-C26	140.71	0.31	0.185		σ*C16-H22	3.07	0.68	0.042
	σ*C26-H32	30.41	0.73	0.133					

Isotropic linear polarizability $\langle\alpha\rangle$, anisotropic linear polarizibility $\Delta\alpha$, first-order hyperpolarizability $\langle\beta\rangle$ and total dipole moment (μ) values were calculated by B3LYP method.

(μ), $\langle\alpha\rangle$, $\Delta\alpha$ $\langle\beta\rangle$ values were calculated by the use of the subsequent equations:[25]

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\langle\alpha\rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = [1/2((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2)]^{1/2}$$

$$<\beta> = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$$

NLO data by the DFT / B3LYP / 6-311 ++ G (d, p) method of p-NA selected as standard with alkylaminophenol compound were shown in Table 4.

Linear polarizability values are negative, indicating that there is a dipole in the opposite direction of the electrical field. Linear polarizability value of selected alkylaminophenol is 2.5 times of p-NA. In anisotropic linear polarizability value is higher than p-NA. When the first order hyperpolarizability values are examined, it is seen that the alkylaminophenol compound is lower than the hyperpolarizability value of p-NA.

Table 4. NLO values of the alkylaminophenol compound

Property	p-NA	B3LYP	Property	p-NA	B3LYP
μ_x	-7.4519	-1.5179	β_{xxx}	-99.4560	-35.7077
μ_y	-0.001	1.3048	β_{xyy}	16.7004	18.5251
μ_z	0.6869	1.0776	β_{xzz}	12.9992	-13.0982
μ	7.4835 Debye	2.2733 Debye	β_{yyy}	-0.0012	16.9110
α_{xx}	-58.7480	-141.5996	β_{xxy}	-0.0004	-29.8279
α_{yy}	-53.2767	-150.3433	β_{yzz}	0.0001	2.6038
α_{zz}	-60.6128	-148.7810	β_{zzz}	0.4969	12.0045
$<\alpha>$	-8.52×10^{-24} esu	-2.18×10^{-23} esu	β_{xxz}	12.9100	-2.9584
			β_{yyz}	0.4172	3.7631
$\Delta\alpha$	9.79×10^{-25} esu	1.20×10^{-24} esu	$<\beta>$	8.99×10^{-31} esu	2.98×10^{-31} esu

Alkylaminophenol compound can be considered worthy of study as a material for NLO applications according to results and suggested for the second-order non-linear optical research.

3.4 Thermodynamic properties

Some thermodynamic parameters of alkylaminophenol compound have been calculated in the previous study.[7]

In our study, the heat capacity, $C^0_{p,m}$, entropy, S^0_m and enthalpy, H^0_m values were calculated[26,27] under 1 atm pressure at different temperature values varying from 100 to 500 K) and the results obtained are listed in Table 5.

Correlation dependencies are also given in Figure 2.

Table 5. Temperature dependence of thermodynamic properties of the alkylaminophenol compound

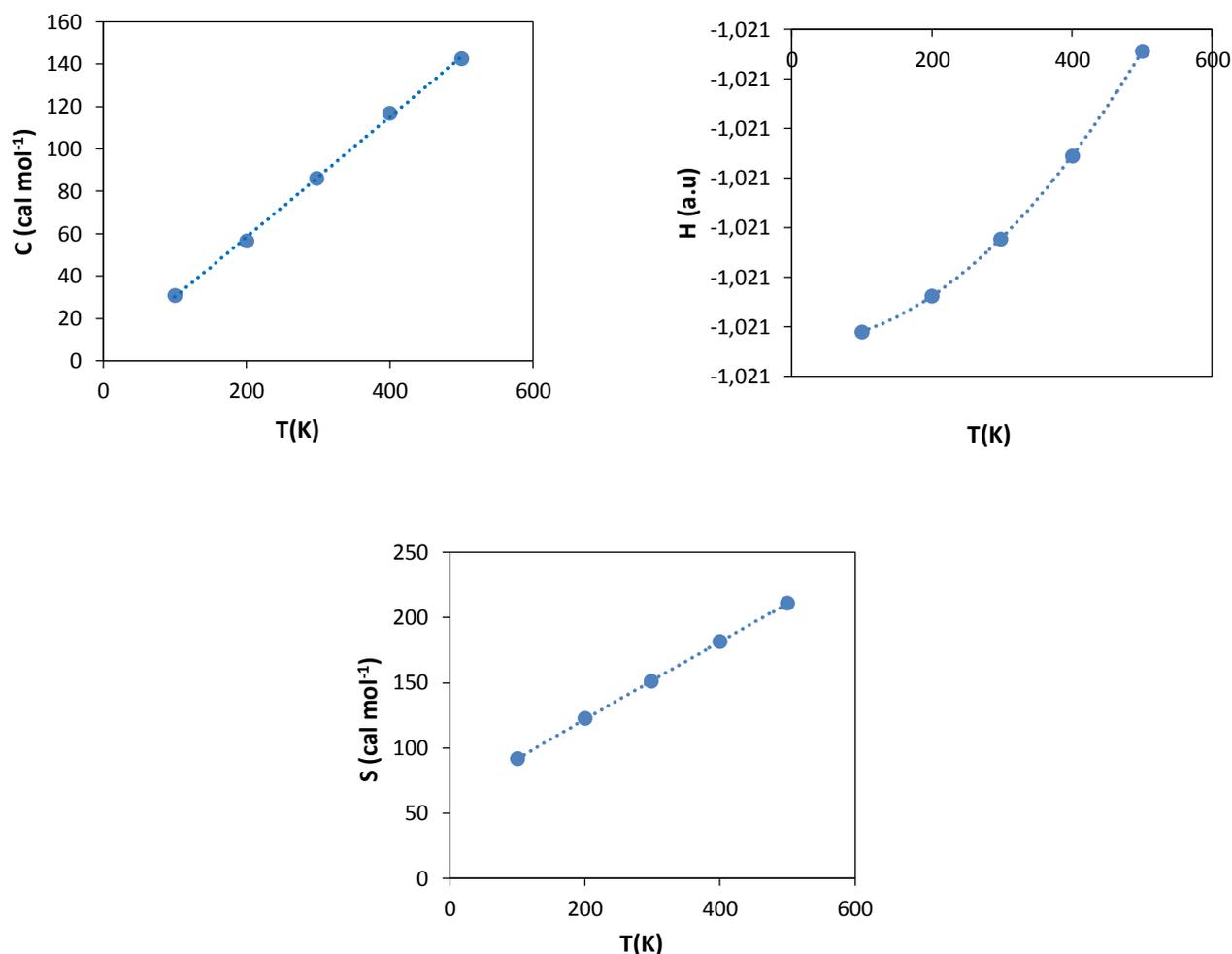| Temperature (K)	Heat Capacity (C)	Entalpy (H)	Entropy (S)
100	30.947	-1021.3010	91.857
200	56.727	-1021.2937	122.353
298.15	86.184	-1021.2823	151.194
400	116.700	-1021.2655	181.437
500	142.635	-1021.2443	210.796

Figure 2. Correlation graph for thermodynamic parameters of 2-(Azepan-1-yl(naphthalen-1-yl)methyl)phenol compound.

Additionally, the correlation equations as functions of temperature and corresponding correlation coefficients are given below in follows for the 2-(Azepan-1-yl(naphthalen-1-yl)methyl)phenol compound.

C (Cal mol^{-1} K^{-1}) = 1.8991 + 0.282 T + 2 x 10^{-6} T^2 (R^2 = 0.999)

H (a.u)= -1021.3 + 2 x 10^{-6} T + 2 x 10^{-7} T^2 (R^2 = 1)

S (Cal mol^{-1} K^{-1}) = 61.562 + 0.3054 T + 1 x 10^{-5} T^2 (R^2 = 1)

4. CONCLUSIONS

In this study, NPA, NBO, NLO and thermodynamic parameters of the alkylaminophenol compound were calculated by DFT/B3LYP/6-311++G(d,p) method. The natural population analysis has given information about the distribution of electrons to orbitals to understand the structure. The NBO analysis has provided the details of the type of hybridization and the nature of bonding in alkylaminophenol compound. Also, the dipole moment, polarizability, first-order hyperpolarizability values were calculated. A standard material p-NA (p-nitroaniline) was used for NLO properties. Alkylaminophenol compounds can be considered as a material for NLO applications according to the results. In addition, it has been seen with correlations that the temperature is effective on thermodynamic parameters such as enthalpy, entropy, and heat capacity.

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Conflict of interests

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

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