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New comparative theoretical calculations of some N,N-bis[(3,5-dimethylpyrazol-1-yl)methyl]phenylamines tripodal ligands

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Abstract
New comparative theoretical calculations on four synthesized tripodal ligands type organic compounds: N,N-bis[(3,5-dimethylpyrazol-1-yl)methyl]phenylamines (**1-4**) have been carried out with the AM1 level of theory using the GAUSSIAN03 suite of programs. This study was performed in order to elucidate the effect of the moieties nature linked to the aminic nitrogen on the thermodynamic properties of molecules. For all three variables (standard enthalpy, heat capacity, entropy) the investigated substituents are classified in the following order: $(pz)_2N$ (**4**) > CH_3 (**2**) > OH (**3**) > H (**1**). The bis-tripod ligand (**4**) which is characterized by two chelation centers, has the greatest values.

Keywords: Tripod, theoretical calculations, pyrazole.

1. Introduction
Many tripodal ligands have been synthesized in the literature for industrial, biological and medical aims [1-5]. Several papers report the synthesis, the biological and the physico-chemical properties of pyrazolic derivatives such as N,N-bis[(3,5-dimethyl-pyrazol-1-yl)methyl]arylamines [6-10]. Also, correlations between the structural parameters of similar compounds and the inhibiting effects have been described [11]. During the evaluation of the anticancer effect [10] of compounds **1** and **4**, we were surprised by the fact that only the ligand **1** have a very high cytotoxic properties, but compound **4** shows a small activity. This result led us to investigate the influence of the chelation centres number on the thermodynamic properties and to get better informations about these variables, especially when the conjugation phenomenon is present between the phenylic ring and the aminic nitrogen. The molecules examined (figure1) are N,N-bis[(3,5-dimethylpyrazol-1-yl)methyl]-aniline **1**, N,N-bis[(3,5-dimethylpyra-zol-1-yl)-methyl]-p-toluidine **2**, 4-{N,N-bis[(3,5-dimeth -ylpyrazol-1-yl)met-yl]}-aminophen-ol **3** and N,N,N',N'-tetrakis[(3,5-dimethyl-pyrazol-1-yl) -methyl]-p-phenylenediamine **4**. These materials have been already reported in the literature by the condensation of 1-(hydroxymethyl)-3,5-dimethylpyrazole with a series of primary amines such as aniline [12], p-methylaniline [12], p-hydroxyaniline [13] and p-phenylene-diamine [6].

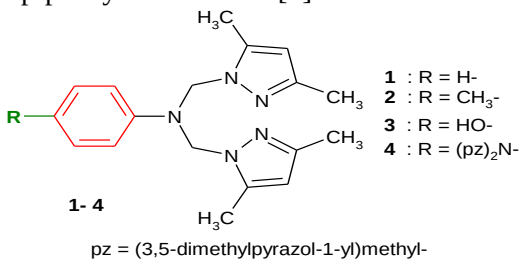

Figure 1. Chemical formula of the investigated compounds

2. Theoretical calculation method

Among theoretical chemical methods for evaluation of thermodynamic properties, AM1 level of theory has some merits. All calculations in this work were carried out with the AM1 level of theory using the GAUSSIAN03 [14] suite of programs. More information about these methods is available elsewhere [15]. The examined thermodynamic properties for the structures are standard enthalpy ($\Delta H = H° - H°_{298.15}$, in kJ mol^{-1}), heat capacity (C_p at constant pressure in kJ mol^{-1} K^{-1}) and entropy (S in J mol^{-1} K^{-1}). These variables are calculated versus temperature.

3. Results and discussion

3.1. Thermodynamic properties

We have performed theoretical calculations to present a viable structure for the products **1-4**. The fits were performed according to the equations (Table 1) implemented by the National Institute of Standards and Technology [16]. These were fitted to the shomate equations [16] which are implemented by the JANAF tables of the NIST databases. These equations converged to an R^2 value of 0.999 on average. These equations have been very good at predicting physical properties of various molecules, as we have tested in the past [17-20].

Table 1. Thermodynamic properties of compounds **1-4**

		Fitted Thermodynamic Equation (T/1000=t)	100 K	298.15K	1000 K
1	C_p	-29.11626 + 1434.84389*t -583.70994*t^2 + 11.28844*t^3 + 0.57394*t^{-2}	165.45	350.07	835.67
	S	920.04362*ln(t) + 1157.95467*t -2211.71407*t^2/2 + 965.39069*t^3/3 -7.42815/(2*t^2) + 418.85752	441.66	702.14	1414.55
	ΔH	-84.28006*t + 1673.22295*t^2/2-918.72808 *t^3/+161.16784*t^4/4 -1.28915/t + 24.18619	10.94	61.40	509.31
2	C_p	-18.71788 + 1477.49373 *t -561.55363 *t^2 -11.01498 *t^3 + 0.56892 *t^{-2}	179.78	374.31	888.7
	S	-39.83295 *ln(t) + 1543.51077 *t + -609.09177 *t^2/2 - 14.59978 *t^3/3 -0.95925 /(2*t^2) + 277.58593	472.65	753.59	1511.32
	ΔH	116.38626 *t + 980.388 *t^2/2 + 5.89791 *t^3/3 + -204.11304 *t^4/4 + 1.16605 /t + -15.53458	12.01	66.35	542.63
3	C_p	-14.82751+ 1458.5308*t -613.3247*t^2 +25.21849 *t^3 + 0.48247*t^{-2}	172.71	368.38	857.77
	S	-189.63902*ln(t) + 1739.876*t +1.66877*t^2/2 -850.43555 *t^3/3 -3.22946/(2*t^2) -0.6108	449.74	724.87	1461.74
	ΔH	302.21827*t + 488.2964*t^2/2 -0.51511*t^3/3 +110.18311 *t^4/4 +4.8683/t -67.94157	11.25	64.57	526.93
4	C_p	-22.7965+ 2423.88078*t -918.88496*t^2 -21.03716*t^3 +0.8802*t^{-2}	297.56	621.58	1465.2
	S	-224.09296*ln(t) + 3013.63222*t -1117.38142*t^2/2 - 317.42147 *t^3/3 -3.57765/(2*t^2) + 19.71838	652.32	1119.43	2371.92
	ΔH	-115.67866*t + 2823.96614*t^2/2 -1478.51484*t^3/3 +227.79696 *t^4/4 -2.08535/t +37.92212	19.15	109.51	896.31

3.2. Effect of the R substituents on the thermodynamic properties

We examine now the effect of moieties linked to the aminic nitrogen towards thermodynamic properties of molecules. The obtained results show a difference of standard enthalpy, heat capacity and entropy variables. We could consider the important effect of substituents linked to the phenylic ring, has on the thermodynamic properties of molecules. As can be seen from figures 2-4, the substituents have a large effect on the standard enthalpy, heat capacity and entropy values.

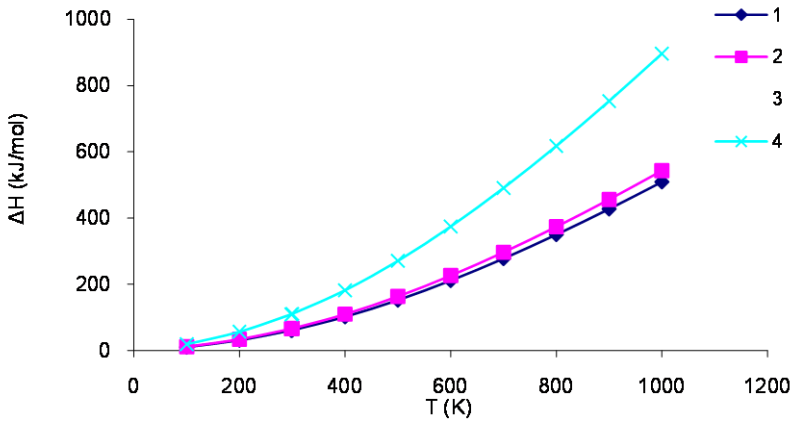

Figure 2. Standard enthalpy of compounds **1-4**.

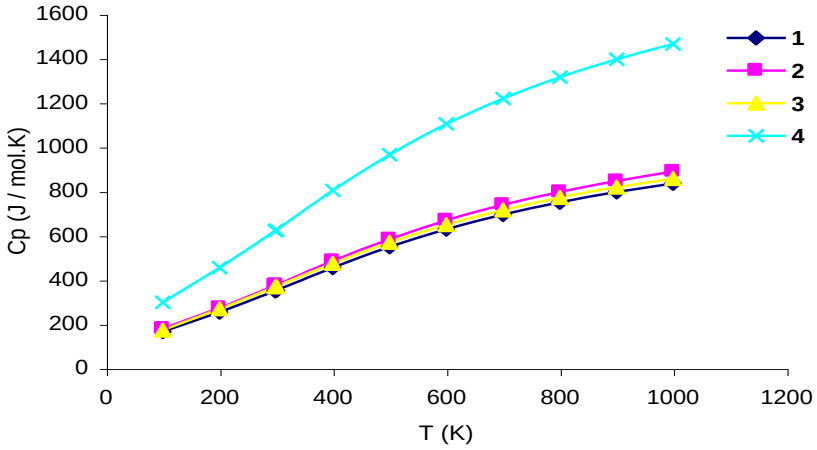

Figure 3. Heat capacity of compounds **1-4**

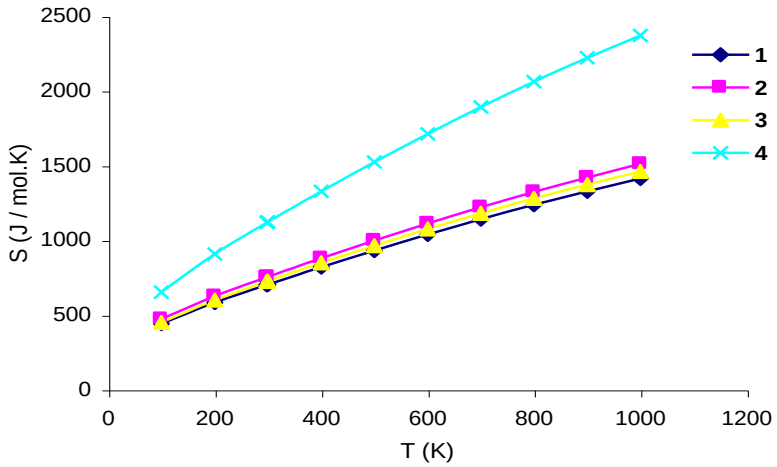

Figure 4. Entropy of compounds **1-4**.

Among these compounds, N,N,N',N'-tetrakis[(3,5-dimethylpyrazol-1-yl)methyl]-p-phen- ylenediamine **4** has the greatest values of heat capacity, entropy and standard enthalpy. The N,N-bis[(3,5-dimethylpyrazol-1-yl)-meth-yl]aniline **1** has the lower thermodynamic properties. Two groups of compounds will be distinguished. In the case where the phenylic ring is linked to the H, CH_3, and OH moieties **1-3:** The thermodynamic properties order for the studied molecules is **2** (R = CH_3) > **3** (R = OH) > **1** (R = H). These minor differences will be associated to the electron-donating ability of the R substituents. The inductive (R = CH_3) and mesomeric (R = OH) effects have not given a significantly differences between the values of these variables. At room temperature (298.15K) the replacement of the hydrogen by the methyl group, increases the heat

capacity of 24.24 J mol^{-1} K^{-1}, and while it is changed by the hydroxyl group the increases values is 18.31 J mol^{-1} K^{-1}. For the other variables the increasing are respectively 22.75 J mol^{-1} K^{-1}, 51.45 J mol^{-1} K^{-1} for the entropy and 4.95 kJ mol^{-1}, 3.17 kJ mol^{-1} for the standard enthalpy. On the other hand, the conjugation phenomenon induced by the oxygen atom in the structure **3**, gives a lower increasing comparatively to the inductive effect observed in the molecule **2**. In the case where the phenylic ring is linked to an other aminic nitrogen $N(pz)_2$ **4**, our data shows that this compound presents a very high thermodynamic variables values. The bis-tripod ligand **4** has a thermodynamic value two fold more than the mono-tripod compound **1**. These results show that the heat capacity, entropy and standard enthalpy values are also influenced by the chelating centre numbers and the donor effect of pyrazolyl groups. This comparative study has encouraged us to find probably a link between the anti-cancer activity [10] and the thermodynamic properties.

Conclusion

In conclusion, the theoretical calculations reported in this paper demonstrate that the thermodynamic properties such as standard enthalpy, heat capacity and entropy depend strongly on the substituents linked to the phenylic ring. These N,N-bis[(3,5-dimethylpyrazol-1-yl)methyl]phenylamines has a very high standard enthalpy, heat capacity and entropy values when the phenylic ring is linked to the bis[(3,5-dimethylpyrazol-1-yl)methyl]amine **4**. Thus, the number of chelating centers and the inductive effect increase considerably the values of thermodynamic variables. These results may be have potential relevance for understanding the physico-chemical and biological properties of the N,N-bis(3,5-dimethyl-pyrazol-1-ylmethyl)phenylamines tripodal ligands.

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