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On the Configuration of 2,2′-Bipyridyl and 5,5′-Bis-Isoxazole by Means of the CNDO/2 Method

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The conformation of 2,2′-bipyridyl and 5,5′-bis-isoxazole is studied by the CNDO/2 method. Calculations suggest that the trans configuration is more stable than the cis for both systems. For 2,2′-bipyridyl a minimum for a non planar form is inferred.

In a previous paper [1], the possibility of a theoretical calculation of the stability of different conformations for molecules like biphenyl, 2,2′-bipyridyl and 5,5′-bis-isoxazole was investigated.

The method [2] consisted in considering the total molecular energy as a sum of non-bonded interaction energy (σ-energy) and π-electronic energy, calculated with the usual PPP technique [3]. As we have already pointed out [1], such a procedure cannot give reliable informations on non planar configurations.

A semiempirical method, which has found wide applications, is the CNDO/2 method developed by Pople, Santry and Segal [4, 5, 6]. It does not involve any hypothesis on the $\sigma - \pi$ separability condition [3] and was employed by Tinland in a conformational study of biphenyl [7]. We thought it interesting to apply the same method (by making use of the QCPE version [8] of it) to 5,5′-bis-isoxazole and 2,2′-bipyridyl in order to compare the results with our previous ones. The geometry of these molecules was the same as in Ref. [1], and bond distances and angles were kept constant during the rotation. In Tables 1 and 2 the total energies of 2,2′-bipyridyl and 5,5′-bis-isoxazole, respectively, are reported as functions of the dihedral angle (ϑ) between the planes of the two rings.

The results for the first molecule (Table 1) show a flat minimum for the molecular energy in the ϑ range 45–90°, while the trans configuration ($\vartheta = 0°$) is found more stable than the cis ($\vartheta = 180°$) by about 2 Kcal/mole. As for 5,5′-bis-isoxazole (Table 2), no minimum in the whole range of ϑ and a maximum near $\vartheta = 90°$ are observed ($\Delta E_{0°-90°} \sim 3$ Kcal/mole). Again the trans configuration appears to be more stable than the cis by ~ 1 Kcal/mole.

These results are quite similar to our previous ones [cases (b) and (c) of Table IV], Ref. [1]), while the small energies involved are much more in agreement with the experimental behaviour of these molecules [9, 10]. Of course, some of the con-

Table 1. *Total energy of 2,2' bipyridyl as a function of* ϑ

ϑ (degrees)	0	30°	45°	60°	90°	120°	150°	180°
	trans							*cis*
$-E$ (a.u.)	100.3396	100.3404	100.3408	100.3408	100.3407	100.3403	100.3387	100.3361

Table 2. *Total energy of 5,5'-bis-isoxazole as a function of* ϑ

ϑ (degrees)	0	30°	60°	90°	120°	150°	180°
	trans						*cis*
$-E$ (a.u.)	105.7719	105.7707	105.7686	105.7675	105.7682	105.7695	105.7705

siderations made in Ref. [1] on the reliability of semiempirical methods in this kind of problems still apply, but the CNDO/2 seems to give, at least in these cases, results not in complete disagreement with experiment.

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