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Note

CNDO/2 Calculation of Dipole Moments of *trans*-1,2-Dipyridylethylenes

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Recently, the dipole moments of the six isomeric *trans*-1,2-dipyridylethylenes (DPE) have been reported¹. With the exception of 1,2-di-(pyridyl-4)-ethylene (4,4-DPE) all isomers can exist in several configurations depending on the relative position of the two nitrogen atoms. Thus, for the six *trans*-isomers, 15 non-identical configurations are possible² (Fig. 1). In the determination and discussion of the observed dipole moment, the knowledge of the amount of each configuration present in the measured sample is of great importance. Two procedures have so far been used to obtain this information.

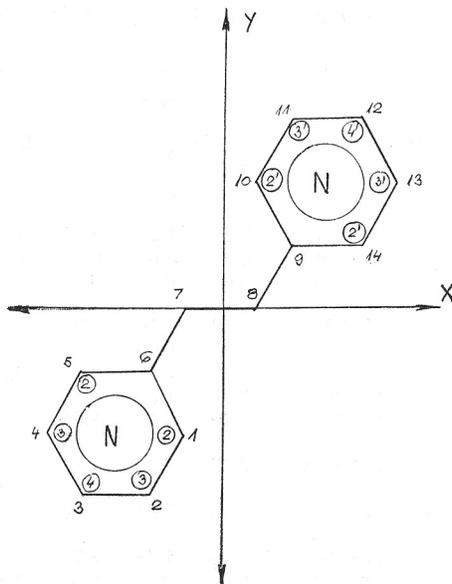


Fig. 1. Geometry and numbering scheme of isomeric *trans*-dipyridylethylenes. Inner numbers in circles correspond to the positions of nitrogen in accordance with chemical notation.

In the first procedure the fraction (x_i) of the configuration present can be determined comparing the experimental dipole moment (μ) with the dipole moments of each configuration (μ_i) calculated by vector addition of the corresponding pyridine ring dipole moments. Namely, for the measured orientation polarization of the mixture P_{og} we have

$$P_{og} = x_1 P_{o1} + x_2 P_{o2}$$

with

$$P_{io} = \mu_i^2/0.128 T$$

where the orientation polarization of each configuration, P_{oi} , can be obtained from its calculated dipole moment μ_i (T = absolute temperature). Thus, if only two configurations are present, x_1 and x_2 are readily accessible.

In the second procedure, the photochemical *trans-cis* isomerization followed by photocyclodehydrogenation to corresponding phenanthrolines^{3,4} is carried out, and the amount of the *trans*-DPE configuration initially present is related to the composition of the final phenanthroline mixture. Unfortunately all conformations having a nitrogen at the position of cyclization cannot yield phenanthrolines and their amount is thus undeterminable.

Both procedures yield information about the presence of different configurations in the measured samples. Although the vector addition method showed good agreement when practically only one configuration was present, its weak point is that it is completely empirical and too crude to distinguish between all possible configurations. For this reason CNDO/2 type calculations^{5,6} of all 15 configurations of the six *trans*-DPE isomers were performed and the dipole

TABLE I
Dipole Moments of trans-1,2-Dipyridylethylenes

DPE	Configuration	CNDO Energy (a. u.)	Dipole moments					Vector addition	Composition %	
			CNDO			Exp.				
			D _x	D _y	D _{tot}					
2-2'	1-14; 5-10	-115.8074	3.27	1.97	3.82	1.70	3.98	18 ^a		
	5-14	-115.8146	0.0	0.0	0.0					
	1-10	-115.8185	0.0	0.0	0.0					82 ^a
2-3'	5-11; 2-14	-115.7996	2.58	3.46	4.31	3.28	4.60	32 ^a		
	1-13; 4-10	-115.8011	3.91	0.40	3.93					
	5-13; 4-14	-115.8057	0.64	1.55	1.68					2.24
1-11; 2-10	-115.8183	0.70	0.49	1.64						
2-4'	1-12; 3-10	-115.8005	3.25	1.88	3.75	4.00	3.98	100 ^a		
	5-12; 3-14	-115.8080	0.03	3.88	3.88					
3-3'	2-13; 4-11	-115.7894	3.20	1.88	3.71	2.57	3.98	42 ^{a,b}	56.5 ^b	
	4-13	-115.7984	0.0	0.0	0.0					
	2-11	-115.8072	0.0	0.0	0.0					0.0
3-4'	3-11; 2-12	-115.7914	2.55	0.40	2.59	2.34	2.29	57 ^b		
	4-12; 3-13	-115.7985	0.65	2.27	2.36					43 ^b
4-4'	3-12	-115.7942	0.0	0.0	0.0	0.16	0.0	100		

^{a)} from experimental and vector-addition dipole moments; ^{b)} from phenanthroline yields.

moments of each configuration determined. CNDO/2 calculations which take into account all valence electrons have so far proved very reliable in calculating dipole moments. The details of the calculation can be found in ref. 7. Listed in Table I are the non-equivalent configurations of the 6 DPE isomers together with their CNDO energies, CNDO dipole moments, experimental dipole moments, vector addition dipole moments and their compositions as obtained either from the latter two quantities or from phenanthroline yields. As usual for CNDO/2 calculations the energy differences are a great deal too high, but they do give a feeling about the relative position of the molecules on an energy scale. The CNDO/2 dipole moments obtained show that the vector addition approach was justified in the present case and indicate the reliability of the reported composition (Table I last column).

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IZVOD

CNDO/2 račun dipolnih momenata *trans*-1,2-dipiridiletena

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Šest izomernih *trans*-dipiridiletena (DPE) mogu postojati u ukupno 15 različitih konfiguracija: tri 2,2'-DPE, četiri 2,3'-DPE, dvije 2,4'-DPE tri 3,3'-DPE i dva 3,4'-DPE. Za 4,4'-DPE postoji samo jedna moguća konfiguracija. Uspoređivanje računatih dipolnih momenata pojedinih konfiguracija pomoću CNDO/2 metode s eksperimentalnim vrijednostima za pojedine izomere ukazuje na udjele tih konfiguracija u smjesi. Ovi se udjeli slažu s rezultatima dobivenim na osnovu metode vektorske adicije i iz prinosa produkta fotociklizacije.

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