A Conformational Analysis of the Six Isomers of Bipyridinium Dication

Ellak I. von Nagy-Felsobuki

Department of Chemistry, University of Newcastle,
Newcastle, N.S.W. 2308, Australia

Received June 22, 1987

The conformational analysis of the bipyridinium dications have been investigated using ab initio STO-3G calculations in which the inter-ring bond length was optimized at each torsional angle. The variation of the inter-ring separation has been rationalized using a heuristic valence bond model (which is electrostatic in nature) and which was suggested by the molecular orbital calculations. Furthermore, all six isomers show a double potential minima at the optimium torsional angles of ~ 50° and ~ 130° respectively. Moreover, all barrier heights are calculated to be less than 8 kJ mol^{-1}, thereby suggesting that the barrier heights are not large enough to prevent rapid interconversion between different rotamers.

J. Heterocyclic Chem., **25**, 33 (1988).

1. Introduction.

The diquaternary salts of bipyridine and their radical cations have been extensively studied [1-2] in order to unravel their herbicidal activity [1], their use as redox indicators [2] and their application in solar energy collection and storage systems [3]. The dications are of particular interest since they have the ability to form stable and intensely coloured radical cations by reversible reduction. Their herbicidal activity is due to the production of the superoxide radical anion caused by regeneration of the dication by air [1-2]. The conformation analysis of the dications plays an important role since a planar structure is postulated to be an important prerequisite for active dication derivatives [1-2].

For several 1,1'-dimethyl-4,4' -bipyridines high-resolution diffraction studies have been reported [4-5]. The molecular dimensions of the bipyridinium dications for the dichlorides, dibromides, diiodies and tetracyanonickelate are in excellent agreement with each other. These studies show that the crystal structures of the bipyridinium dications are planar, with the two pyridine rings being distorted hexagons (as in the case for pyridine) and the inter-ring separations being 0.146, 0.145, 0.148 and 0.147 nm respectively.

Similar studies of diquat dications (2,2'-bipyridinium dications with a 1,1'-ethylene bridge) indicate that the molecule adopts a twisted *trans* conformation in the solid state with the torsional angle of ~20° [6-8]. Moreover, the diprotonated molecules also adopt a twisted *trans* conformer but with the torsional angle being somewhat larger (30-40°) [9-11]. The latter conformer is consistent with ultraviolet [12-13], nmr [14] and Raman [15] studies in the liquid phase. So far, there has been no reported analogous conformational or crystal structure studies for the 2,3'-, 2,4'-, and 3,4'-bipyridinium dications.

There have been a number of theoretical studies of the rotational isomers of the bipyridinium dications using semi-empirical [16-17] and all electron methods [18-20]. Recently, von Nagy-Felsobuki [18] studied the rotational isomer of 4,4'-bipyridinium dication using an all-electron STO-3G basis set method. The lowest calculated energy conformer is twisted (45.3°), with an optimized inter-ring bond length of 0.1522 nm and a barrier height of 5.86 kJ mol^{-1}. On the other hand, for both 4,4'- and 2,2'-bipyridinium dications Hoffmann *et al.* [19,20] using the same method and basis set, reported more extensively optimized conformations. For the 4,4'- and 2,2'-bipyridinium dications their calculations yielded twisted lowest energy conformers with (torsional angles, inter-ring bond distance) of (44.7°, 0.1522 nm) and (138.1°, 0.1516 nm) respectively [19-20].

It is the purpose of this study to theoretically analyze the conformational behaviours of the bipyridinium dications on internal rotation and inter-ring distance optimization, thereby contributing to a better understanding of their structural properties.

2. Details of the Calculations.

The all-electron energies have been computed using the LCAO MO SCF restricted Hartree-Fock method within the GAUSSIAN 82 suite of programmers [21] and using the internal STO-3G (s = p) basis set. This level of theory is moderately successful in reproducing geometrical parameters of closed-shell molecules [22] and moreover, in the case of the mono-substituted benzene is even more successful in predicting rotational barriers than the internal split valence basis sets [23].

A partial flexible rotor model was used in this investigation. That is, the ring geometry was fixed ($R_{C\text{-}N}$ = 1.34 Å, $R_{N\text{-}H}$ = 1.008 Å, $R_{C\text{-}H}$ 1.08 Å and $R_{C\text{-}C}$ = 1.39 Å) and adopted from the X-ray diffraction studies of the salts of 1,1'-dimethyl-4,4'-bipyridinium dications [1]. To keep the calculations tractable, the Fletcher-Powell [24] algorithm was used in optimizing the $R_{C\text{-}C}$ bond length. Table 1 lists the optimlized $R_{C\text{-}C}$ bond lengths for all six isomers as a function of the torsion angle and Table 2 gives the net

Mulliken charge distributions for *cis* and *trans* conformers at selected atomic sites.

Table 1

Optimized Inter-ring $R_{C\text{-}C}$ Bond Lengths (/nm) [a]

Angle (/Deg) [b]	2,2′	2,3′	3,3′	2,4′	3,4′	4,4′
0	0.15557	0.15459	0.15441	0.15390	0.15331	0.15420
30	0.15349	0.15289	0.15271	0.15251	0.15204	0.15251
60	0.15303	0.15256	0.15231	0.15239	0.15198	0.15217
90	0.15342	0.15297	0.15270	0.15284	0.15243	0.15252
120	0.15286	0.15252	0.15231	0.15239	0.15198	0.15217
150	0.15296	0.15278	0.15263	0.15251	0.15204	0.15251
180	0.15448	0.15435	0.15419	0.15390	0.15331	0.15420

[a] Using the Fletcher-Powell routine [24]. [b] An angle of zero degrees denotes *cis* configuration.

Table 2

Net Mulliken Charge Distribution of *Cis* and *Trans* Bipyridinium Dications at Selected Atomic Sites [a]

Dication [b]		*Ipso* Carbons		Ring Nitrogens		*N*-Hydrogen	
2,2′	0	0.183	0.183	−0.258	−0.258	0.322	0.322
	180	0.187	0.187	−0.254	−0.254	0.318	0.318
2,3′	0	0.189	0.020	−0.259	−0.240	0.303	0.338
	180	0.190	0.019	−0.258	−0.240	0.310	0.340
3,3′	0	0.025	0.025	−0.242	−0.242	0.334	0.334
	180	0.023	0.023	−0.241	−0.241	0.335	0.335
2,4′	0	0.183	0.075	−0.254	−0.242	0.313	0.342
3,4′	0	0.018	0.081	−0.243	−0.246	0.335	0.337
4,4′	0	0.075	0.075	−0.244	−0.244	0.330	0.330

[a] The *ipso* carbons are the carbons connected by the inter-ring bond. The *N*-hydrogens are the hydrogens bonded to the ring nitrogens. The two pyridine rings are labelled by the absence and presence of a dash. [b] The bipyridinium dications are labelled according to the respective positions of the ring nitrogens. The *cis* conformer is labelled by a zero torsion angle, whereas the *trans* conformer is labelled by the torsional angle of 180°.

The torsional potentials of molecules are usually fitted to a cosine Fourier series of the form [25-26],

$$\triangle V(\varnothing) = \sum_j \tfrac{1}{2} V_j (1 - \cos j\varnothing)$$

In the case of torsional potentials that are periodic and symmetric (in the sense that $V(\varnothing) = V(\pi + \varnothing)$) only even values of j are allowed, whereas for unsymmetric torsional potentials all values of j are required. Table 3 lists the optimized energies and various potential parameters for all six isomers.

3. Results and Discussion.

Table 1 highlights that for the *cis* and (where applicable) the *trans* conformers the variation of the $R_{C\text{-}C}$ bond length follows the sequence: 2,2′ > 2,3′ > 3,3′ ~ 4,4′ > 2,4′ > 3,4′. The sequence can be rationalized using a simple heuristic valence bond model in conjunction with the MO calculations.

Table 3

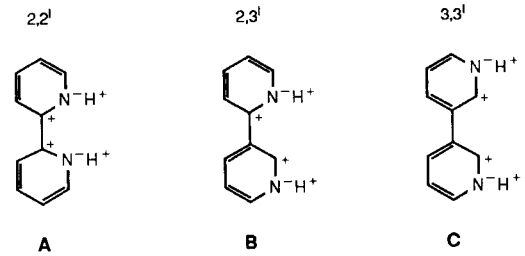
Relative Energies and Flexible Rotor Potential Constants for Bipyridinium Dications [a]

	2,2′	2,3′	3,3′	2,4′	3,4′	4,4′
ΔE (30°)	−21.13	−16.43	−15.30	−12.55	−10.96	−12.51
ΔE (60°)	−30.75	−21.96	−19.64	−13.61	−10.82	−13.98
ΔE (90°)	−29.77	−19.39	−16.11	− 9.14	− 6.16	− 9.97
ΔE (120°)	−34.98	−22.94	−19.20	−13.61	−10.82	−13.98
ΔE (150°)	−32.30	−19.02	−15.39	−12.55	−10.96	−12.51
ΔE (180°)	−18.01	− 4.09	− 1.23	0.0	0.0	0.0
V_0	−26.32	−16.96	−14.37	−10.24	− 8.29	−10.49
V_1	−13.87	− 3.19	− 0.31	− −	− −	− −
V_2	−17.94	−14.71	−13.05	− 6.80	−4.01	− 7.63
V_3	− 3.19	− 0.71	− 0.70	− −	− −	− −
V_4	−13.87	−12.49	−12.03	−11.35	−10.41	−11.02
V_5	− 0.96	− 0.19	− 0.21	− −	− −	− −
V_6	− 2.82	− 2.63	− 2.45	− 2.35	− 2.15	− 2.34
θ (/deg)	54.39	50.30	48.85	44.85	43.39	45.39
θ′ (/deg)	133.23	131.63	131.48	135.15	136.61	134.61
R_e (/Å)	0.15316	0.15248	0.15229	0.15231	0.15189	0.15219
R_e (/Å)	0.15302	0.15253	0.15231	0.15231	0.15189	0.15219
[b] $\Delta E_{Barrier}$	1.23	3.38	4.69	6.78	7.37	6.04
[b] $\Delta E'_{Barrier}$	6.97	4.78	4.22	6.78	7.37	6.04
[c] $\Delta E_{Barrier}$	1.11	2.59	3.65	5.29	5.92	5.64
[c] $\Delta E'_{Barrier}$	5.69	3.70	3.22	5.29	5.92	5.64

[a] All numbers in the body of the table are in units of kJ mol^{-1} unless otherwise stated. [b] Obtained by fitting the Fourier series - see body of text. [c] Obtained by fitting a cubic spline [30].

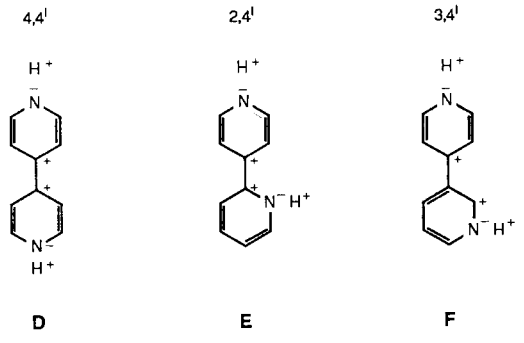
For all the six isomers the STO-3G calculations predict: an excess of electron density on the nitrogens, electron density depletion on the hydrogens bonded to the nitrogens as well as on the *ipso* carbons. This is summarized in Table 2 which gives net Mulliken population analysis at these atomic sites. Furthermore, the results given in Table 2 are generally consistent with a CNDO/2 calculations reported elsewhere [16].

For the unsymmetrical conformers the STO-3G calculations suggest that the following canonical structures are of importance:



Assuming that each ring is a pyridinium ring (*i.e.* only a single charge is delocalized within each ring) then structures **A**, **B** and **C** would generate a further eight canonical structures. Moreover, on simple electrostatic grounds the predicted inter-ring separation would be given by the sequence: 2,2′ > 2,3′ > 3,3′. Such a sequence would be independent of the torsional angle. This is exactly what is predicted by the STO-3G calculations given in Table 1.

For the symmetrical bipyridinium dications the variation of inter-ring separation is more complicated because of the delicate balance between the two opposing mechanisms; steric versus conjugation. Nevertheless, the MO calculations suggest that the most important canonical structures are of the form:



D **E** **F**

Once again (assuming each ring is a pyridinium ring) one can generate another three equivalent canonical structures from **D** and eight from structures **E** and **F**. It is clear that structure **D** is weighted ~2.3 times more important then either structures **E** and **F**. Furthermore, on simple electrostatic grounds, structure **E** would yield a longer $R_{C\text{-}C}$ bond when compared to **F**. Hence this simple heuristic valence bond model would predict that the inter-ring separation (no matter what the torsional angle) would be given by the sequence: 4,4′ > 2,4′ > 3,4′. Whilst this is exactly the STO-3G prediction for the *cis* and *trans* conformers, for torsional angles between 30° and 120° the sequence 4,4′ < 2,4′ occurs. This reflects the need to take into consideration not only electrostatic effects but also the delicate balance between steric and hyperconjugative effects.

Whilst small differences between the inter-ring separation of the *cis*-3.3′- and 4,4′-isomers can be explained in terms of canonical structures (which suggest that only the 4,4′-isomer can exhibit conjugation between the two rings) the *trans* conformers suggest that the conjuation effects are much smaller than the electrostatic effect. This is suggested because the inter-ring distance for the *trans*-3,3′-bipyridinium dication is only 0.00001 nm less than that of the 4,4′-bipyridinium dication.

In the work on 4,4′ biprydinium dication, it was shown [18] that the potential constants calculated from a data set of torsional angles in steps of 10° intervals were accurately reproduced by a truncated data set based on torsional angles in steps of 30°. Moreover, it was also found that the V_6 term was required in order to more accurately model the potential barrier. The latter was in accord with Barone *et al.* [27] investigation of 4,4′ bipyridine. Consequently, Table 3 gives the relative potential constants for all six isomers of the bipyridinium dications based on the conclusions reached in a previous report [18].

For the 4,4′-bipyridinium dication the truncated set of torsional angles results in an increase of 0.18 kJ mol^{-1} in the barrier height (*i.e.* $\triangle E_{Barrier} = E_{cis} - E_{90°}$) with the optimium torsional angle changing little (0.01°) (see Table 3 and reference [18]). Moreover, compared with the more extensively optimized structure of Hoffmann *et al.* [19-20], the torsional angle and barrier height of 4,4′ bipyridinium dication given in Table 3 is 0.7° larger and 1.16 kJ mol^{-1} smaller respectively. Thus the calculation presented here are in excellent accord with previously reported results.

The STO-3G calculations predict that all six isomers possess a second minimum. This is clearly shown in Figure 1 which gives the variation of the relative energy of all six isomers with torsional angle.

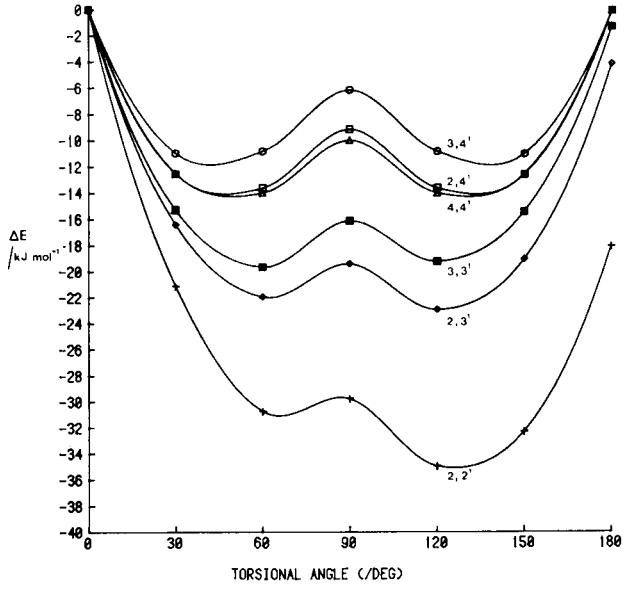


Figure 1. Plot of the flexible rotor relative energies of the bipyridinium dications with respect to the planar form as a function of the torsional angle:

2,2′; 2,3′; 3,3′; 2,4′; 3,4′; 4,4′.

Table 3 shows that the (torsional angles, barrier heights) of the symmetrical isomers namely, 2,4′-, 3,4′- and 4,4′-bipyridinium dications are (44.9°, 7.0 kJ mol^{-1}), (43.4°, 7.5 kJ mol^{-1}) and (4.54°, 6.2 kJ mol^{-1}) respectively. The barrier heights yield the sequence of : 4,4′ < 2,4′ < 3,4′ which is in accord with the variation of the inter-ring separations of the planar structures (see Table 1).

In the case of the unsymmetrical isomers, for both the 2,2'- and 2,3'-bipyridinium dication the transoid structure gives the global minimum, whereas the second minimum is the cisoid structure. Table 3 highlights that for 2,2'- and 2,3'-bipyridinium dications the (torsional angle, barrier heights) for cisoid conformers are (54.4°, 1.2 kJ mol^{-1}) and (50.3°, 3.4 kJ mol^{-1}) respectively, whereas the transoid conformers yield (133.23°, 7.0 kJ mol^{-1}) and (131.6°, 4.5 kJ mol^{-1}) respectively. This is essentially in agreement with experiment [6-15] and with variations in the inter-ring separations. For 3,3'-bipyridinium dication Table 3 shows that the cisoid (and not the transoid) structure gives the global minimum. That is, the (torsional angle, barrier height) for cisoid and transoid structures are (48.9°, 4.7 kJ mol^{-1}) and (131.5°, 4.2 kJ mol^{-1}) respectively. The small differences in the barrier heights of these two conformers is consistent with the nitrogen ring positions. However, the absolute difference is beyond the precision of the calculation although experimental evidence does suggest that the cisoid structure may be the more stable [28].

It is anticipated that the variation of both the total energy and $R_{C\text{-}C}$ as a function of the torsion angle reflect the same competing mechanisms [29]. Hence it would be expected that $R_{C\text{-}C}$ would vary in much the same way as a function of torsion angle as the total energy. Figure 2 shows that the variation of $R_{C\text{-}C}$ yields slow varying but relatively smooth functions and moreover on comparison with Figure 1 follow analogous patterns (*i.e.* symmetric and unsymmetric molecules show a double minima).

It is clear that all six isomers have predicted the torsional angles of ~50 or 130° and barrier heights less than 8 kJ mol^{-1}. Barrier heights are extremely sensitive to the fitting procedure. This is illustrated in Table 3 where for example, fitting a cubic spline [30] to the potential energies yield differences in the barrier height of up to ~1.5 kJ mol^{-1} when compared with the Fourier series fit. Nevertheless whatever the fit, it is clear that the barrier heights of the bipyridinium dications are of the same order of magnitude as the average energy available from the ambient temperature (~2.5 kJ mol^{-1}). This suggests that the barrier heights are not large enough to prevent rapid interconversion between the different rotamers and so places an added focus onto the geometry of the monocation in order to predict the activity in the herbicidal activity [20].

Acknowledgement.

The author wishes to thank Professor L. A. Summers for many valuable discussions and Mr. S. Dunne for his assistance in the preparation of some of the calculations. All of the STO-3G calculations were performed on VAX 11/780 and 8550, Computer Centre, University of Newcastle. The primary graphics was generated on an Apple II computer and associate plotter which was obtained from support of the Senate Research Committee, University of Newcastle.

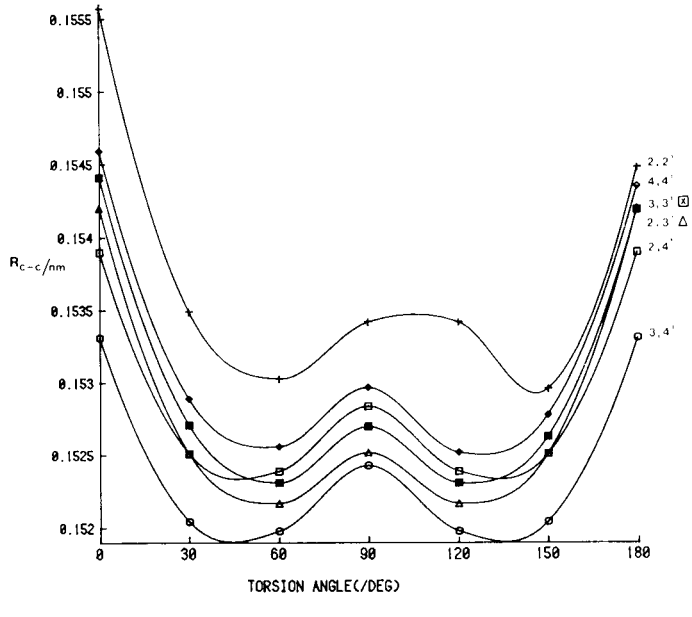


Figure 2. Plot of the difference between the optimized bond lengths as a function of torsional angle.

REFERENCES AND NOTES

[1] L. A. Summers, "The Bipyridinium Herbicides", Academic Press, New York, 1980.

[2] L. A. Summers, *Advan. Heterocyclic Chem.*, **35**, 281 (1984).

[3] A. Graetzel, *Acc. Chem. Res.*, **14**, 376 (1981).

[4] S. S. Basson, C. D. L. Bok and J. G. Leipoldt, *Acta. Crystallogr. Sect.* **B,25**, 579 (1969).

[5] J. H. Russel and S. C. Wallwork, *Acta. Crystallogr. Sect.* **B,28**, 1527 (1972).

[6] J. E. Derry and T. A. Homer, *Nature*, **221**, 464 (1969).

[7] T. Sundaresan and S. C. Wallwork, *Acta. Crystallogr. Sect.* **B,28**, 3065 (1972).

[8] P. D. Sullivan and M. L. Williams, *J. Am. Chem. Soc.*, **98**, 1711 (1976).

[9] S. Koda, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Japan*, **44**, 1597 (1971).

[10] B. C. Wang and A. W. Cordes, *Inorg. Chem.*, **9**, 1643 (1970).

[11] C. Belin, J. Roziere and J. Potier, *Acta. Crystallogr. Sect.* **B,37**, 1306 (1981).

[12] R. H. Linnell and A. Kaczmarczyk, *J. Chem. Phys.*, **65**, 1196 (1961).

[13] D. K. Hazara and S. C. Lahiri, *Z. Phys. Chem.*, **257**, 497 (1976).

[14] S. Castellano, H. Gunther and S. Ebersole, *J. Phys. Chem.*, **69**, 4166 (1965).

[15] D. J. Barker, R. P. Cooney and L. A. Summer, private communications (1987).

[16] J. Burdon, M. H. B. Hayes and M. E. Pick, *J. Environ. Sci. Health*, **B12**, 37 (1977).

[17] R. Benedix, P. Birner and H. Hennig, *J. Mol. Struct.*, **90**, 65 (1982).

[18] E. I. von Nagy-Felsobuki, *Chem. Phys. Letters*, **127**, 245 (1986).

[19] H. J. Hoffmann, R. Cirmirglia and J. Tomasi, *J. Chem. Res.* (s), 48 (1987).

[20] H. J. Hoffmann, R. Cimiraglia and J. Tomasi, *J. Mol. Struct.*, **139**, 213 (1986).

[21] J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder and J. A. Pople, GAUSSIAN 82, Carnegie-Mellon University, (1982).

[22] J. A. Pople, "Applications of Electronic Structure", H. F. Schaefer 111, ed, Plenum Press, New York, 1977.

[23] S. Marriott and R. D. Topsom, *Aust. J. Chem.*, **39**, 1157 (1986).

[24] R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963).

[25] K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

[26] L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973).

[27] V. Barone, F. Lelj, L. Commisso, N. Russo, C. Cauletti and N. Piancastelli, *Chem. Phys.*, **96**, 435 (1985).

[28] L. A. Summer, private communication (1987).

[29] J. Almlöf, *Chem. Phys.*, **6**, 135 (1974).

[30] G. Forsythe, M. A. Malcolm and G. B. Moler, "Computer Methods for Mathematical Computations", Prentice-Hall, New York, 1977.