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A QUANTUM-MECHANICAL STUDY ON THE STEREOCHEMISTRY OF THE ISOMERIC BIPYRROLES, BIFURANS, BITHIOPHENES, THIENYLFURANS AND BISELENOPHENES

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Abstract—The most probable conformational arrangements of isomeric bipyrroles, bifurans, bithiophenes, thienylfurans, and biselenophenes have been investigated using the Extended Hückel MO approach. The barrier heights between the *syn* and *anti* forms decrease sharply on going along the series bifurans, bithiophenes, and biselenophenes. The barrier height for the interconversion *syn* ↔ *anti* follows the trend: 2,2′ > 2,3′ > 3,3′. The energy difference between the *syn* and *anti* conformers is small (except in the case of 2,2′-bifuran). Planar *syn* conformation is predicted more stable than *anti* for 2,2′- and 2,3′-isomers (except for 2,3′-biselenophene), while the 3,3′-isomers are predicted to have *anti* conformation more stable than *syn*. The tendency to assume a nonplanar conformation at the equilibrium is shown by 1,1′-bipyrrole, 2,3′-biselenophene, 3,3′-bithiophene and 3,3′-biselenophene.

For the two energetically most favourable conformations of each molecule the charge distribution is calculated using the CNDO/2 method.

INTRODUCTION

In previous papers we have analysed theoretically the conformational problem of heteroaromatic systems formed by two cycles linked together by essentially single bonds, namely two 6-membered rings[1] and one 6- and one 5-membered ring.[2] Now we have turned our attention to systems resulting from the connection of two 5-membered heterocycles: bipyrroles, bifurans, bithiophenes, thienylfurans, and biselenophenes; in all 17 molecules. The chemistry and physical properties of some of these compounds have been the object of extensive investigations[3a] in view of the fact that they enter as groups in important naturally-occurring compounds;[3b] for example bithiophene derivatives have been found as constituent parts in the roots of *TAGETES MINUTA L.* or in plant *ECLIPTA ALBA*. On the other hand, experimental structural investigations are lacking for all of these molecules but the bithiophenes, for which the electron diffraction[4, 5] and X-ray[6] analysis and electric dipole measurements[7–9] have been reported.

A thorough quantum-mechanical investigation on the problem of their stereochemistry has, therefore, more than passing interest. Such an objective has been pursued with interesting results for two of these systems (2,2′- and 3,3′-bithiophene) by Skancke[10] through the calculation of the total energy estimated as the sum of the π-delocalization energy, the core repulsion energy and the Van der Waals interactions.

Generally speaking, these systems may be planar *syn*, planar *anti* or twisted to some angle around the central single bond; they might also behave as nearly free rotors. Clearly, their conformational preferences are governed by the opposite roles exerted by the π-electron conjugation and the non-bonded (NB) repulsions resulting from H ... H short contacts and from the presence of lone pairs on the heteroatoms. The attempt to rationalise the relative importance of these two factors is, therefore, the main aspect of this analysis.

COMPUTATIONAL DETAILS

In view of the great difficulty in attempting non-empirical calculations on molecules of this size we have adopted semi-empirical methods. Use has been made of the EH-MO method,[11] since a wide experience on a number of organic, biological, and inorganic compounds[12] testifies the reasonable ability of this method to challenge conformational problems. The *s* and *p* valence orbitals of C, N, O and S have been given. Slater exponents. The orbital exponents of Se have been derived from Burns rules[13] and the 1s orbital of H has been given the exponent 1·3. The VOIP'S have been taken from Hoffmann and Imamura[14] for H, C, N and O, and from Hinze and Jaffé[15] for S and Se. No use has been made of the d-orbitals on S and Se in view of the minor role played by these orbitals in bonding as shown recently by an *ab-initio* treatment on thiophene[16] and by EH-MO results on phenyl-thiophenes.[2]

Idealized structures have been formed by connecting the actual geometries of the 5-membered heterocycles (as derived from microwave investigations[17]) with a bond directed along the line bisecting the angles in the two rings. This inter-ring bond has been given the length of 1·470 Å, except in the case of 1,1'-bipyrrole where a more adequate value of 1·445 Å has been adopted.

The potential energy function of each molecule has been calculated with respect to the variation of the angle of twist around the coannular linkage in the range 0°–180° with a scanning of 10°. The results are plotted in the Figs 1–5.

Since the CNDO/2 method provides more reliable atomic charges than the EH-MO method, especially for heteroatomic systems, the charge distribution for the two more favourable conformations of each molecule has been determined with the aid of the former treatment. The parametrisation has been taken from Sichel and Whitehead[18] (IP's and one-centre two-electron Coulomb integrals) and from Burns[13] (orbital exponents for all orbitals but the 1s of H where a value of 1·2 has been assumed). The beta integrals have been calculated using the standard Wolfsberg–Helmholtz formula[19] with $K = 1$ and the two-centre two-electron Coulomb integrals using the Ohno relation.[20] The results obtained are presented in Tables 1–5. As far as we are aware, the present CNDO/2 calculations on biselenophenes appear to be the first ones of this kind on Se heterocycles.

DISCUSSION

First of all, it must be emphasized that in view of the approximate nature of the adopted method the results obtained are not to be given an absolute value: their main significance is in the *trends* that are provided. Secondly, three different situations can be distinguished between the various isomers of a given molecular system with respect to the steric factors that appear (at least qualitatively) to be mostly operative

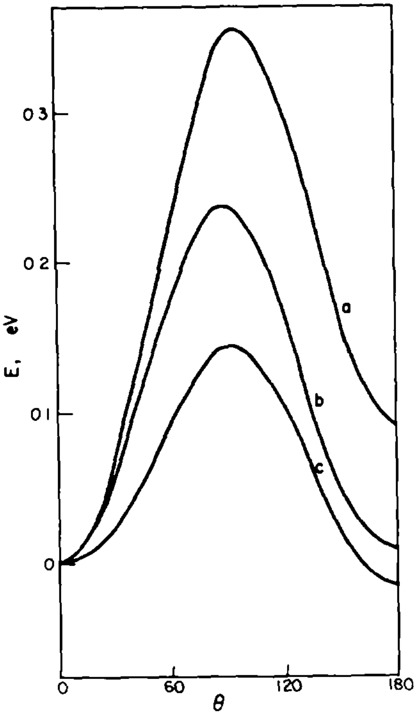


FIG 1. Extended Hückel energy *vs* angle of twist (θ) for 2,2'-bifuran (a), 2,3'-bifuran (b) and 3,3'-bifuran (c). The energy zero has been arbitrarily assigned to the planar *syn* conformation.

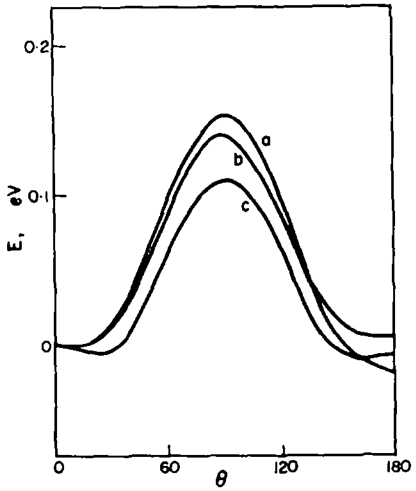


FIG 2. Extended Hückel energy *vs* angle of twist (θ) for 2,2'-bithiophene (a), 2,3'-bithiophene (b) and 3,3'-bithiophene (c). The energy zero has been arbitrarily assigned to the planar *syn* conformation.

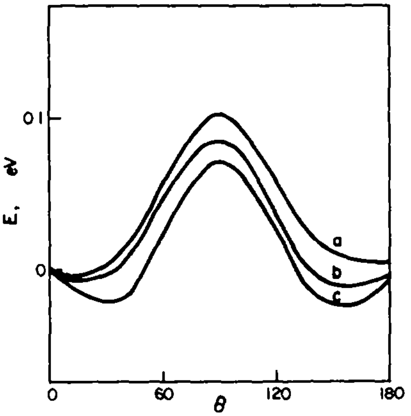


FIG 3. Extended Hückel energy *vs* angle of twist (θ) for 2,2'-biselenophene (a), 2,3'-biselenophene (b) and 3,3'-biselenophene (c). The energy zero has been arbitrarily assigned to the planar *syn* conformation.

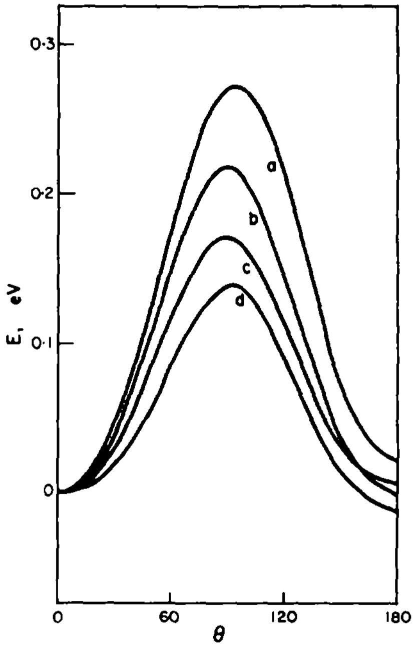


FIG 4. Extended Hückel energy *vs* angle of twist (θ) for 2,2'-thienylfuran (a), 3,2'-thienylfuran (b), 2,3'-thienylfuran (c) and 3,3'-thienylfuran (d). The energy zero has been arbitrarily assigned to the planar *syn* conformation.

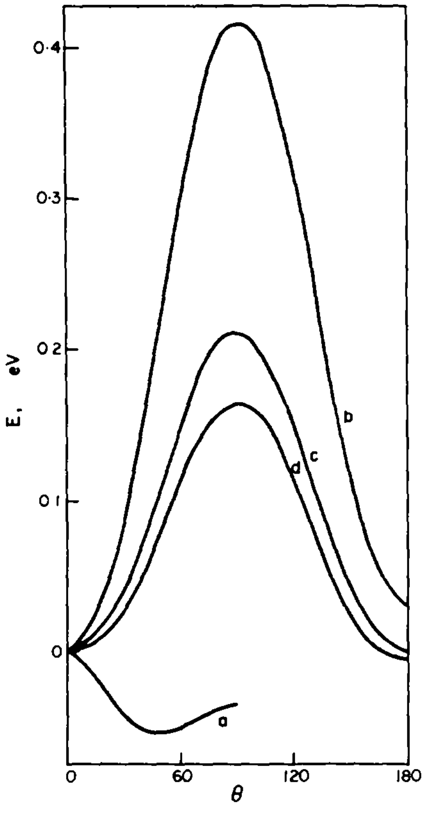


FIG 5. Extended Hückel energy *vs* angle of twist (θ) for 1,1'-bipyrrole (a), 2,2'-bipyrrole (b), 2,3'-bipyrrole (c) and 3,3'-bipyrrole (d). The energy zero has been arbitrarily assigned to the planar *syn* conformation.

in determining the stereochemistry in co-operation with the conjugative factor. The 2,2'-isomer is characterized by one short H... H contact and the NB interaction between the lone pairs on the heteroatoms in the *syn* conformation and by the NB interactions between lone-pairs and H atoms in the *anti* conformation. On the other hand, two short H... H contacts are operative in both the *syn* and *anti* geometries of the 3,3'- isomer. In view of the H atom attached to the nitrogens all the bipyrroles present this state of affairs. Finally, the 2,3'-isomer displays one short H... H contact and the NB interaction between the lone-pair on the heteroatom at the position 2 and the proximate H atom of the other ring in both the *syn* and *anti* arrangements. Thirdly, a complete check of the present findings with the experimental information is out of question since there are only very few data available and most of these refer to the bithiophenes. Thus a definitive check of some predictions presented must await further experimental proofs.

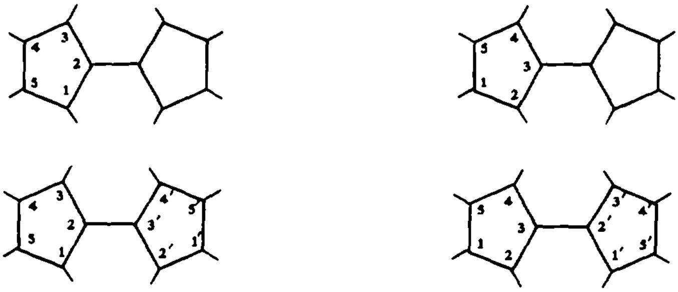
The following conclusions emerge:

(i) An inspection of the Figs 1–3 reveals that the barrier heights between the *syn* and *anti* forms decrease sharply on going along the series bifurans, bithiophenes, and biselenophenes, with a marked collapse in the first step. This means that along

TABLE 1. NET ATOMIC CHARGES OF BIFURANS*

Isomer	2,2′		3,3′		2,3′	
Twist angle	0°	180°	0°	180°	0°	180°
Atom						
O-1	−0·320	−0·325	−0·306	−0·307	−0·334	−0·327
C-2	0·255	0·247	0·151	0·157	0·271	0·271
C-3	−0·117	−0·108	0·004	0·001	−0·124	−0·129
C-4	−0·080	−0·077	−0·108	−0·114	−0·077	−0·077
C-5	0·191	0·190	0·202	0·205	0·185	0·185
H-2			0·015	0·017		
H-3	0·029	0·033			0·027	0·025
H-4	0·027	0·025	0·028	0·027	0·024	0·025
H-5	0·015	0·015	0·014	0·014	0·013	0·013
O-1′					−0·307	−0·304
C-2′					0·178	0·167
C-3′					−0·028	−0·020
C-4′					−0·101	−0·098
C-5′					0·205	0·201
H-2′					0·022	0·018
H-4′					0·030	0·035
H-5′					0·016	0·015
μ(D)	1·509	0	1·183	0	1·282	0·442

* The twist angle is measured from the planar *cis* conformation. Atom numbering is assumed to be as follows:



this series the deviation from planarity causes a variation on the energetic contribution stemming from π-conjugation between the two rings, which tends to be progressively compensated by a concomitant release of strain energy, *i.e.* the conjugative factor tends to become less important. Leaving aside the precise values of the barrier heights to interconversion *syn* ↔ *anti* (which cannot be provided by this very approximate method), we can however deduce some information from a comparative analysis of these barriers. Whereas the bifurans are readily anticipated to be able to assume only rigid (or quasi-rigid) structures, an easy interconversion between the preferred conformers of the bithiophenes and biselenophenes, *i.e.* a nearly free internal rotation, can be hardly excluded.

TABLE 2. NET ATOMIC CHARGES OF BITHIOPHENES*

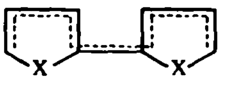
Isomer	2,2′		3,3′		2,3′	
Twist angle	0°	180°	26°	158°	0°	180°
Atom						
S-1	0·093	0·112	0·114	0·114	0·093	0·099
C-2	0·037	0·037	−0·084	−0·081	0·045	0·046
C-3	−0·091	−0·101	0·028	0·027	−0·099	−0·104
C-4	−0·055	−0·054	−0·085	−0·087	−0·056	−0·055
C-5	−0·046	−0·049	−0·034	−0·033	−0·051	−0·054
H-2			0·022	0·023		
H-3	0·024	0·017			0·021	0·019
H-4	0·018	0·017	0·021	0·019	0·016	0·015
H-5	0·020	0·021	0·018	0·018	0·018	0·019
S-1′					0·121	0·123
C-2′					−0·084	−0·071
C-3′					0·020	0·019
C-4′					−0·080	−0·091
C-5′					−0·031	−0·031
H-2′					0·021	0·027
H-4′					0·025	0·019
H-5′					0·021	0·020
μ(D)	2·026	0	1·355	0·222	1·781	0·656

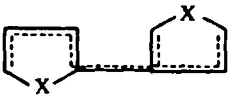
* See note below Table 1

These results agree satisfactorily with the following evidence. Electron diffraction data on the gaseous phase support such a hypothesis for 2,2′-bithiophene[4] and yield a barrier height of approximately 2 kcal/mole for 3,3′-bithiophene.[5] The behaviour of the bithiophenes under charge-transfer conditions also suggests almost free rotation of the thiophene rings around the central bond.[21] Previous calculations by Skancke[10] indicate nearly free rotation for both these isomers. On the other hand, experimental evidence of strong conjugation between the two rings in 2,2′-bifuran is provided by the marked bathochromic shift in its UV spectrum compared to furan.[22]

(ii) The barrier height for the interconversion *syn*↔*anti* follows the trend: 2,2′ > 2,3′ > 3,3′. This variation is clearly diagnostic of a different reluctance of the three isomeric systems to lose π-conjugation between the two rings, which should also change in the above order.

A support of this point of view might be found in the marked hypsochromic displacement observed in the UV spectra[23] of the bifurans and bithiophenes when compared with the 2,2′-isomer. The effect can be recognised also by taking into account π-electron lattices like the following:





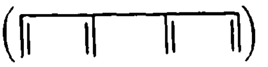
where the progressive branching in the "polyenic system" virtually present in each of the three isomers causes a decrease in the conjugation between the two moieties.

TABLE 3. NET ATOMIC CHARGES OF BISELENOPHENES*

Isomer	2,2′		3,3′		2,3′	
Twist angle	15°	180°	38°	157°	20°	160°
Atom						
Se-1	−0·015	−0·005	0·001	0·002	−0·022	−0·019
C-2	0·072	0·067	−0·060	−0·055	0·076	0·076
C-3	−0·077	−0·080	0·044	0·040	−0·087	−0·089
C-4	−0·041	−0·040	−0·068	−0·070	−0·040	−0·039
C-5	−0021	−0·022	−0·005	−0·006	−0·026	−0·027
H-2			0·033	0·034		
H-3	0·027	0·026			0·025	0·024
H-4	0·024	0·023	0·025	0·025	0·022	0·022
H-5	0·031	0·031	0·030	0·030	0·030	0·029
Se-1′					0·007	0·009
C-2′					−0·049	−0·045
C-3′					0·036	0·037
C-4′					−0·061	−0·067
C-5′					−0·006	−0·005
H-2′					0·035	0·036
H-4′					0·028	0·027
H-5′					0·032	0·031
μ(D)	3·614	0	2·252	0·408	3·218	1·603

* See note below Table 1.

As a matter of fact, evidence in this sense is offered by the strong hypsochromic effect observed in the UV spectra[24] on going from 1,3,5,7-octatetrane

 *to 2,3-divinyl-butadiene*  *system.*

(iii) With the exception of 2,2′-bifuran, the energy difference between the *syn* and and *anti* conformers is found to be relatively little and in some instances even negligible. This means that the relative importance of the steric factors (mentioned at the beginning) operative in the *syn* and *anti* conformations, respectively, is comparable. The anamalous behaviour of 2,2′-bifuran suggests that in this case the NB interactions between the lone-pairs on the O atoms (*syn* conformation) are less repulsive than the NB interactions between one lone-pair and one H atom (*anti* conformation). This, in turn, could be explained by claiming the less diffuseness of the lone-pair on the O atom than those on the S and Se atoms.

According to electron diffraction findings on 3,3′-bithiophene[5] the *anti* (not coplanar) conformer is more stable than the *syn* (not coplanar) conformer by approximately 0·3 kcal/mole. Also the Skancke calculations[10] on this molecule favour slightly the *anti* conformer. The present result for 2,2′-bithiophene agrees well with the slightly different heats of atomisation calculated for the *syn* and *anti* conformers,[25] which indicate the *anti* conformer as being the more stable only by *ca* 0·3 kcal/mole.

TABLE 4. NET ATOMIC CHARGES OF THIENYLFURANS*

Isomer	2,2′		3,3′		2,3′		3,2′	
Twist angle	0°	180°	0°	180°	0°	180°	0°	180°
Atom								
S-1	0·124	0·117	0·123	0·120	0·097	0·105	0·124	0·129
C-2	0·016	0·006	−0·085	−0·078	0·038	0·042	−0·059	−0·071
C-3	−0·087	−0·074	0·030	0·028	−0·091	−0·100	−0·002	0·003
C-4	−0·055	−0·057	−0·086	−0·091	−0·056	−0·054	−0·079	−0·074
C-5	−0·046	−0·043	−0·032	−0·030	−0·045	−0·049	−0·031	−0·034
H-2			0·022	0·025			0·031	0·026
H-3	0·022	0·028			0·021	0·018		
H-4	0·020	0·019	0·022	0·020	0·018	0·018	0·024	0·029
H-5	0·022	0·023	0·020	0·020	0·021	0·021	0·023	0·022
O-1′	−0·338	−0·324	−0·311	−0·312	−0·308	−0·308	−0·339	−0·335
C-2′	0·268	0·270	0·141	0·145	0·146	0·161	0·286	0·285
C-3′	−0·121	−0·134	0·016	0·015	0·002	−0·001	−0·138	−0·140
C-4′	−0·077	−0·076	−0·116	−0·119	−0·107	−0·118	−0·077	−0·077
C-5′	0·185	0·184	0·202	0·203	0·204	0·206	0·178	0·179
H-2′			0·015	0·017	0·015	0·020		
H-3′	0·030	0·024					0·027	0·025
H-4′	0·025	0·024	0·028	0·026	0·031	0·026	0·022	0·022
H-5′	0·012	0·013	0·011	0·011	0·014	0·013	0·010	0·011
μ(D)	1·701	0·536	1·269	0·049	1·768	0·764	1·298	0·285

* See note below Table 1.

(iv) As to the tendency to assume a non-planar conformation at the equilibrium, the following cases are observed. No preference is exhibited by the bifurans: only a slight aptitude is recognised in the 3,3′-isomer of bithiophene and a certain tendency is displayed by the 2,3′ and 3,3′ isomers of biselenophene. This theoretical behaviour could be accounted for by advocating that the release in strain energy arising from deviation from planarity exceeds the loss of π-conjugation energy between the two rings on going along the series bifurans, bithiophenes and biselenophenes.

The two flat minima at around 25° and 160° from the planar *syn* form found in the present work for 3,3′-bithiophene agree satisfactorily with the experimental evidence. Indeed, according to electron diffraction analysis 3,3′-bithiophene in the gas phase has two conformers, twisted by about 30° and 150° from the planar *syn* conformation.[5] Also, the analysis of the ESR spectrum of the 2,2′-bithiophene radical anion demonstrates the existence (ESR time scale) of two planar or nearly planar rotational isomers.[26]

In the solid state the isomeric bithiophenes are planar.[6] Electron dipole measurements support a non-planar conformation in solution for the 2,2′ and 3,3′ isomers[7, 8] and a coplanar conformation for the 2,3′ isomer.[7] UV spectral data recorded in non-polar solvents indicate a non-planar conformation for 2,2′-bithiophene,[27, 28] a planar one for 3,3′-bithiophene and a nearly planar one for 2,3′-bithiophene.[28] One must however not attach too much significance to these sources of conformational

TABLE 5. NET ATOMIC CHARGES OF BIPYRROLES*

Isomer	1,1′		2,2′		3,3′		2,3′	
Twist Angle	0°	47°	0°	180°	0°	180°	0°	180°
Atom								
N-1	−0·020	−0·022	−0·231	−0·220	−0·203	−0·205	−0·234	−0·229
C-2	0·047	0·049	0·136	0·135	0·029	0·035	0·156	0·158
C-3	−0·079	−0·079	−0·107	−0·117	0·009	0·008	−0·120	−0·126
C-4	−0·079	−0·079	−0·074	−0·074	−0·108	−0·113	−0·076	−0·075
C-5	0·047	0·049	0·070	0·071	0·080	0·081	0·065	0·064
H-1			0·153	0·159	0·152	0·153	0·153	0·156
H-2	0·020	0·019			0·011	0·014		
H-3	0·022	0·022	0·023	0·016			0·020	0·017
H-4	0·022	0·022	0·019	0·018	0·021	0·018	0·016	0·015
H-5	0·020	0·019	0·011	0·012	0·009	0·009	0·008	0·009
N-1′							−0·201	−0·200
C-2′							0·036	0·048
C-3′							−0·012	−0·013
C-4′							−0·098	−0·109
C-5′							0·084	0·084
H-1′							0·155	0·156
H-2′							0·011	0·017
H-4′							0·025	0·017
H-5′							0·012	0·011
μ(D)	0	0	4·033	0	2·375	0	4·380	3·105

* See note below Table 1.

information not pertinent to the gaseous phase, according to the classical example of biphenyl which shows different conformations in different aggregation states.

(v) The energy patterns of the thienylfurans (Fig 4) reflect the main aspects of the related bifurans and bithiophenes. In particular, the high barriers found suggest difficult interconversion between the conformers *syn* and *anti*. If one considers the barrier to rotation as an index of the degree of conjugation between the two rings, then one has the trend: 2,2′ > 3,2′ > 2,3′ > 3,3′, which nicely parallels the displacement toward longer wavelengths observed in the UV spectra.[23] No tendency to deviate from planarity is shown by any of these systems, for which the most favourable geometry is *syn*, with the exception of the 3,3′-isomer where the *anti* form is preferred.

(vi) The energy curves of 2,2′-, 3,3′-, and 2,3′-isomer of bipyrrole (Fig 5) parallel closely those of the related bifurans. Then the same arguments as to barrier height and conformational preferences can be applied here. It must be recalled, however, that in the case of the bipyrroles the stereochemistry is determined by an over-all compromise between π-interaction and solely short H ... H contacts.

The energy minimum found at around 48° for 1,1-bipyrrole is readily interpreted in terms of mere shortening of the central bond (being a N—N instead of a C—C bond): there is serious steric hindrance between proximate H atoms in the fully-planar conformation.

Incidentally we can mention that there has been one estimate of 25–29° twist for similar compound, pyridinium cyclopentadienide.[29]

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