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MO CALCULATIONS ON THE PREFERRED CONFORMATION AND ELECTRONIC STRUCTURE OF PHENYLPYRIDINES AND BIPYRIDINES

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Abstract—Semi-empirical calculations of the preferred conformations of 2-phenylpyridine, 3-phenylpyridine, 4-phenylpyridine, 2,2'-bipyridine, 3,3'-bipyridine and 4,4'-bipyridine have been performed by means of the extended Hückel method. The ground-state equilibrium geometry is predicted to be *trans*-planar for 2,2'-bipyridine and rotated by some angle around the inter-ring bond for the other molecules, in fair agreement with experimental evidence. The electronic structure and properties of the considered molecules have then been determined by adopting the CNDO/2 approach and the preferred conformation.

A VARIETY of calculations directed toward explaining the twisted ground-state equilibrium conformation of biphenyl in the vapour phase have been appeared in the recent literature.[1–4] In particular, Imamura and Hoffmann[1] carried out an all-valence-electron calculation of the extended Hückel (EH) type and obtained a qualitatively fair agreement with the experimental geometry. Such results have stimulated our interest in exploring the preferred conformation and the electronic properties of some aza-analogs of biphenyl, namely phenylpyridines and bipyridines, for which too the ground-state geometry must be determined by a delicate balance of steric and conjugative factors. Since for only one of these compounds the structure in the vapour phase has been assessed experimentally, (i.e. 4,4'-bipyridine), the most probable configuration can be deduced from EH calculations of the energy of the molecules for various angles of twist around the central bond. The obtained theoretical results are compared with the available experimental evidence and the agreement found satisfactory. Having thus predicted the equilibrium structure, the electronic properties such as the MO energies, the charge distribution and the dipole moment are computed by means of the more sophisticated CNDO/2 method, more reliable in predicting these quantities than the EH theory.

RESULTS AND DISCUSSION

The preferred conformation

2-Phenylpyridine. The ground-state of 2-phenylpyridine (Fig 1) has a shallow minimum at a twist angle of 40°. This theoretical geometry differs significantly from that determined previously by Favini[7] (equilibrium angle of 23°) through a simplified computation of the π-electron energy, the repulsion of the non-bonded atoms and the bonding energy of the σ-bonds. Both of these theoretical angles, however, are in qualitatively fair agreement with experimental evidence. Indeed, a non-coplanarity of the two rings has been suggested in connection with electric dipole measurements in inert solvents:[8] the twist angle is estimated to be at most 40°. A non-planar form with a dihedral angle between the rings of about 30° in inert solvents has also been deduced from NMR parameters[9] and molar Kerr constant measurements.[10]

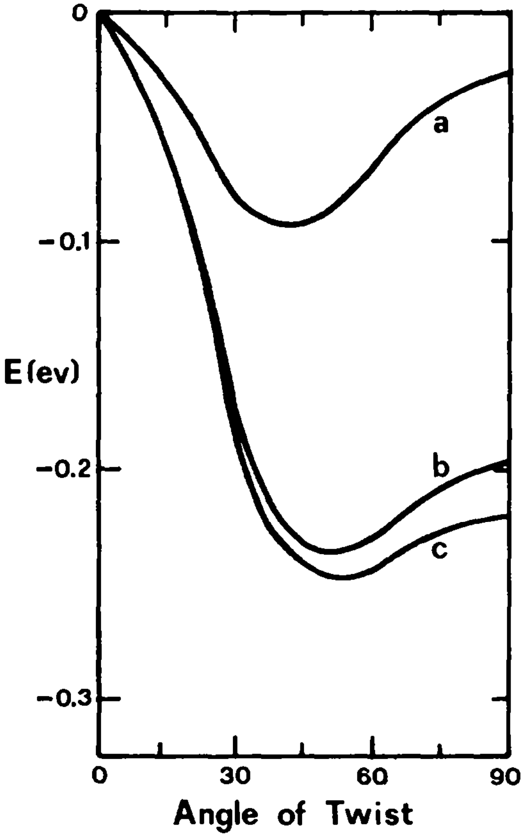

FIG 1. Extended Hückel energy *vs.* angle of twist for 2-phenylpyridine (a), 3-phenylpyridine (b) and 4-phenylpyridine (c). The energy zero has been arbitrarily assigned to the planar conformation.

Among the phenylpyridines 2-phenylpyridine has the least steric problem in a planar geometry, with only one reasonably small H–H contact at a distance comparable to the *ortho–ortho*' interaction in biphenyl. This is reflected in the very low barrier to a planar conformation.

3-*Phenylpyridine*. The potential energy curve of 3-phenylpyridine (Fig 1) has a minimum much deeper than that found for 2-phenylpyridine and at a greater angle of twist (50°). This geometry is consistent with the scarce experimental information, available at present, regarding the conformational stability of the molecule. Indeed a ~ 40° twisted molecule in inert solvents is postulated from electric dipole measurements.[8]

4-*Phenylpyridine*. The present treatment predicts a configuration at twist angle 55° to be the preferred one for 4-phenylpyridine (Fig. 1). Unfortunately, the experimental findings available for this molecule lead to contrasting predictions: a non-coplanar form twisted some 40° around the coannular bond is inferred from electric dipole measurements in inert solvents,[8] while a planar structure is suggested from molar Kerr measurements in inert solvents.[10] So far the present conformational prediction must await further experimental proof.

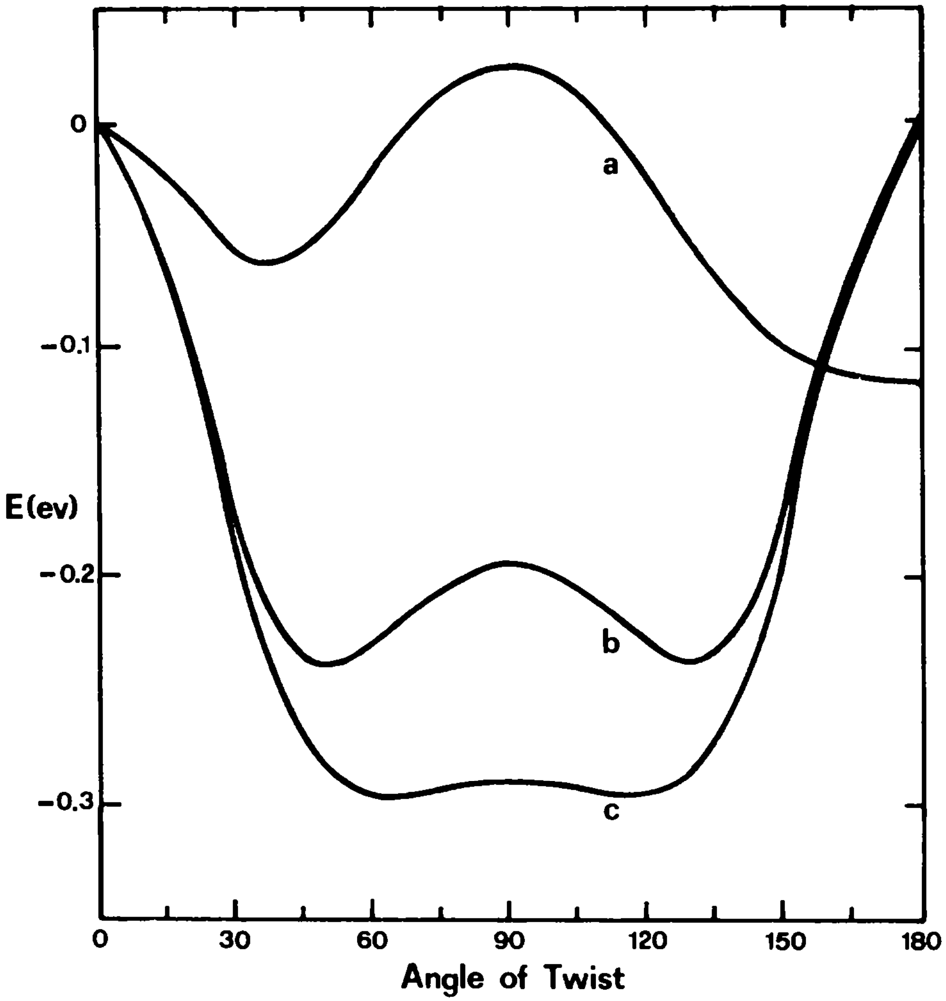

FIG 2. Extended Hückel energy *vs.* angle of twist for 2,2'-bipyridine (a), 3,3'-bipyridine (b) and 4,4'-bipyridine (c). The energy zero has been arbitrarily assigned to the planar *cis* conformation.

2,2'-Bipyridine. As is seen from Fig 2 the EH calculation predicts the *trans*-form to be the most stable configuration of 2,2'-bipyridine. This geometry is in agreement with much experimental evidence. An X-ray diffraction study indicates a *trans*-planar configuration of the two pyridine rings in the solid state.[11] Measurements of electric dipole moment,[12, 13] UV spectroscopic data[14] and NMR parameters[15, 16] are also consistent with a *trans*-planar geometry in inert solvents. On the other hand, the scattering data in the vapour phase are not conclusive;[17] the molecule does not seem to exhibit any well-defined conformation since there seems to be a nearly free rotation through large angle intervals.[18]

The present result agrees also with the conclusion reached by Favini[7] from the calculation with simplified methods of the π-electron energy, the non-bonded interactions and the bending energy of the σ-bonds.

There are two interesting features of the present approach to be noted. Firstly, the *cis* isomer is not predicted to be the unstable species; the unstable species should have a *cisoid* configuration with a dihedral angle about the central bond of 35°. However, the difference in energy between the *cisoid* and *transoid* form is only 0·05 ev (about 1 Kcal/mole): this result may explain the scattering data[18] as well as the relaxation time found in the dielectric investigations.[13] Secondly, the flatness of curve near 180° allows for considerable freedom for oscillation about the planar *trans*-form in agreement with a previous suggestion.[12]

3,3'-Bipyridine. The potential energy curve of 3,3'-bipyridine (Fig 2) exhibits a virtually symmetrical behaviour in the two regions 0° (*cis* form)-90° (perpendicular form) and 90°-180° (*trans* form), showing two nearly equally deep minima at about 50° and 130°. The *cisoid* configuration is postulated to have nearly equal stability with the *transoid* configuration and to be separated from the latter by a low potential barrier (~ 1 Kcal/mole). So far the molecule is predicted to be a nearly free rotor through a large angle interval. This conclusion can be compared, at present, only with NMR evidence, which shows that 3,3'-bipyridine is probably high twisted in all solvents or, alternatively, behaves as essentially free rotor.[16]

4,4'-Bipyridine. The minimum of the energy curve of 4,4'-bipyridine (Fig 2) corresponds to a configuration with a twist angle of 60°, somewhat larger than the equilibrium angle of 37·2° obtained from the electron diffraction results in the gaseous phase.[17] Also IR and Raman data predict a non-coplanar structure.[19] On the other hand, NMR measurements indicate a probably high twist or alternatively a free rotation in all solvents.[16] This latter conclusion appears to be only partially consistent with the rather flat region of low energy between 50° and 90° found in the present calculation.

The overestimation of the equilibrium angle in 4,4'-bipyridine as well as in the parent compound biphenyl[1] can be ascribed to a peculiar characteristic of the EH procedure, *i.e.* the exaggerated importance attached to the steric repulsions with respect to the energy resulting from the π-electron delocalisation. Indeed, on raising the twist angle beyond the "minimum" of the curve the release of π-interaction results in a virtually negligible destabilisation compared with the strong steric interaction associated with lower values of the twist angle. However, although the ground-state conformation postulated for 4,4'-bipyridine is only in rough agreement with the experimental structure, the satisfactory consistence of the theoretical predictions with the experimental findings for the other molecules confirms the general applicability of the EH approach to conformational problems.

Electronic properties

The electronic structure of the molecules under consideration has been investigated using the semi-empirical CNDO/2 method taking into account all valence-electrons and adopting the preferred conformation above established. The most significant results are summarized in Tables 1 and 2.

It is well established that the overall distribution in a molecule is reflected in some measure by its total dipole moment. Within the framework of the Pople–Segal theory,[20] the total dipole moment is calculated as the combination of two contributions, one coming from the atomic charges and the other from the atomic dipoles, including the very important lone-pairs. On this ground, the dipole moment is

TABLE 1. NET ATOMIC CHARGES*

Atom	2-Phenyl pyridine	3-Phenyl pyridine	4-Phenyl pyridine	2,2'-Bipyridine	3,3'-Bipyridine (*cisoid*)	3,3'-Bipyridine (*transoid*)	4,4'-Bipyridine
1	0·268	0·004	0·122	0·238	0·009	0·006	0·116
2	**−0·432**	0·169	−0·101	**−0·423**	0·166	0·168	−0·097
3	0·208	**−0·377**	0·210	0·205	**−0·376**	**−0·375**	0·211
4	−0·085	0·183	**−0·411**	−0·071	0·182	0·184	**−0·408**
5	0·057	−0·059	0·210	0·050	−0·057	−0·056	0·211
6	−0·099	0·017	−0·101	−0·072	0·017	0·015	−0·097
1'	0·037	0·060	0·054	0·238	0·009	0·006	0·116
2'	−0·032	−0·046	−0·040	**−0·423**	0·166	0·168	−0·097
3'	−0·008	0·002	−0·002	0·205	**−0·376**	**−0·375**	0·211
4'	−0·020	−0·029	−0·029	−0·071	0·182	0·184	**−0·408**
5'	−0·010	−0·001	−0·002	0·050	−0·057	−0·056	0·211
6'	−0·021	−0·047	−0·040	−0·072	0·017	0·015	−0·097
H—2		0·012	0·019		0·013	0·012	0·020
H—3	0·009		0·010	0·009			0·012
H—4	0·018	0·011		0·019	0·012	0·012	
H—5	0·010	0·019	0·010	0·012	0·020	0·021	0·012
H—6	0·019	0·013	0·019	0·033	0·013	0·013	0·020
H—2'	0·014	0·014	0·015		0·013	0·012	0·020
H—3'	0·014	0·014	0·015	0·009			0·012
H—4'	0·014	0·014	0·015	0·019	0·012	0·012	
H—5'	0·015	0·014	0·015	0·012	0·020	0·021	0·012
H—6'	0·023	0·014	0·015	0·033	0·013	0·013	0·020

* The bold figures refer to nitrogen atoms. Atom numbering is assumed to be as follows:

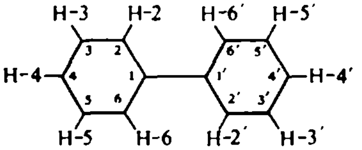

TABLE 2. SOME ENERGY CHARACTERISTICS

Molecule	HOMO (ev)	LEMO (ev)	E_{elec} (a.u.)	E_{tot} (a.u.)
2-Phenylpyridine	−8·733	0·595	−305·6513	−29·8012
3-Phenylpyridine	−8·861	0·722	−305·8210	−29·7979
4-Phenylpyridine	−8·675	0·631	−305·7667	−29·8084
2,2'-Bipyridine	−8·612	0·078	−307·8933	−31·7104
3,3'-Bipyridine (*cisoid*)	−8·941	0·587	−308·0885	−31·7122
3,3'-Bipyridine (*transoid*)	−8·844	0·532	−308·0947	−31·7342
4,4'-Bipyridine	−8·638	0·336	−307·9929	−31·7630

estimated to be 2·50 D for 2-phenylpyridine (exp 1·94 D[8]), 2·71 D for 3-phenylpyridine (exp 2·45 D[8]), and 3·04 D for 4-phenylpyridine (exp 2·57 D[8]). Although the agreement between theoretical and experimental values is not quite satisfactory, the trend turns out to be well preserved. Dipole moments of 4·22 D and 2·76 D are predicted for 3,3′-bipyridine in the *cisoid* and *transoid* configurations respectively.

As far as the energy patterns are concerned, in the twisted compounds the distinction between σ and π MO's is of course no longer strictly valid because of the absence of a symmetry plane. On the other side, the *trans*-planar 2,2′-bipyridine shows an intermingling of σ and π filled levels and a σ–π splitting of the virtual levels, with the π-levels lying just in the frontier region and below the σ; the HOMO (highest occupied molecular orbital) and the LEMO (lowest empty molecular orbital) bear σ and π character respectively and are separated by some 9 ev.

An inspection of the HOMO energies (Table 2) predicts that all the compounds should have remarkably similar electron donor properties (*i.e.* ionization potentials, according to Koopman's theorem). As for the electron acceptor properties (electron affinities), these are expected to be lowest for 3-phenylpyridine of the phenylpyridines and for 4,4′-bipyridine of the bipyridines.

COMPUTATIONAL DETAILS

Before proceeding to the application of the EH method, we felt it desirable to carry out some preliminary calculations of the CNDO/2 type on the phenylpyridines. (The adopted parameterisation is as reported[5]). For these molecules the CNDO/2 method gives an energy minimum at a twist angle of 90°. In view of the serious discrepancy with experimental evidence we have not pursued calculations with this method any further. In connection with this result it is worthwhile to recall that a similar failure of the CNDO/2 approach has been encountered previously by Tinland,[2] who found a very slight minimum for the total energy of the parent hydrocarbon biphenyl at a twist angle of 90°.

Since full details and complete parameterisation of the EH method are given in the original papers,[6] they are not repeated here. An exponent of 1·3 has been assumed for the H 1*s* orbital. The idealized geometry that has been used for all molecules under investigation has perfect hexagonal rings, with C—C and C—N bonds of 1·39 Å; the inter-ring bond is 1·48 Å and the C—H bonds are 1·08 Å.

We have considered in detail the variation of the twist angle, *i.e.* the angle between the planes containing the hexagonal rings, from 0° to 180° (or 90° for symmetrical cases) with a scanning of 15°. Furthermore, some other angles have been explored within the "minimum" regions. The MO calculations have been performed on an IBM 7044 digital computer by using programs written by the authors.

Figs 1 and 2 give a pictorial representation of the results, *i.e.* the calculated total energy *versus* the angle of twist.

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