Tetrahedron. Vol 27, pp. 4947 to 4951. Pergamon Press 1971. Printed in Great Britain

MO CALCULATIONS ON THE PREFERRED CONFORMATION AND ELECTRONIC STRUCTURE OF PHENYL-DERIVATIVES OF PYRROLE, FURAN AND THIOPHENE

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(*Received in the UK* 14 *May* 1971; *accepted for publication* 26 *May* 1971

Abstract—The extended Hückel theory has been applied to the study of the equilibrium conformation of the title compounds. For the predicted geometry the electronic structure and properties have been calculated using the CNDO/2 method.

THERE IS NO experimental information regarding the equilibrium conformation of monophenyl-substituted pyrrole, furan, and thiophene. This unsatisfactory situation warrants therefore both experimental and theoretical investigations. Since the diagnostic use of extended Hückel (EH) calculations[1] has been successfully reported for a variety of conformational problems, we wish to report here some results of EH calculations on the compounds mentioned in order to clarify their preferred geometry.

The AO basis set has been built up of 1s orbital for H (orbital exponent 1·3), of one s and three p orbitals for each C, N, O, and S atoms present (with Slater orbital exponents). The VOIP's have been derived from Hoffman[1, 2] for H, C, N, and O, and from Hinze and Jaffé[3] for S. Bond lengths and angles of the five-membered rings have been taken from microwave studies.[4, 6] An idealized geometry with C—C bonds of 1·39 Å, C—H of 1·08 Å and angles of 120° has been assumed for the Ph ring. The interannular bond has been taken to be 1·40 Å for N-phenylpyrrole and 1·48 Å for all the other compounds.

From the angular dependence of the energy of N-phenylpyrrole (Fig. 1) the greater conformational stability is inferred for a configuration with an angle of twist of about 40°. This result does not agree with the coplanar or nearly so geometry suggested in connection with electric dipole measurements.[7] On the other hand, the barrier to the planar geometry is predicted to be low and nearly half that predicted for biphenyl[8] in accord with the fact that, although the Ph—N distance is shorter than the Ph—Ph bond, the pentagonal ring increases the clearance of the *ortho* H atoms and thus reduces the non-bonded repulsions.

The potential energy curves of the 2-phenyl derivatives of pyrrole (Fig. 1) and furan (Fig. 2) exhibit close analogies, as do those for the 3-phenyl pyrrole and furan. In the case of the 2-substituted molecules the potential functions are relatively flat in the range 0–15° and rise rather sharply above 15°, the slope being greater for the furan derivative in view of its reduced steric hindrance. The most preferred conformation of these compounds is thus presumed to be planar. The particular shape of the curves indicates that for these molecules the decrease in repulsion energy between the *ortho* H atoms resulting from non-planarity does not compensate the concomitant release of π interaction energy. In the case of the 3-substituted compounds, the curves present a shallow

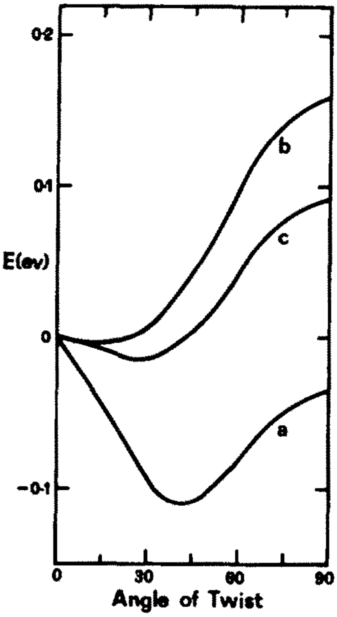

FIG 1. Extended Hückel energy *vs*. angle of twist for N-phenylpyrrole (a), 2-phenylpyrrole (b), and 3-phenylpyrrole (c). The energy zero has been arbitrarily assigned to the planar conformation.

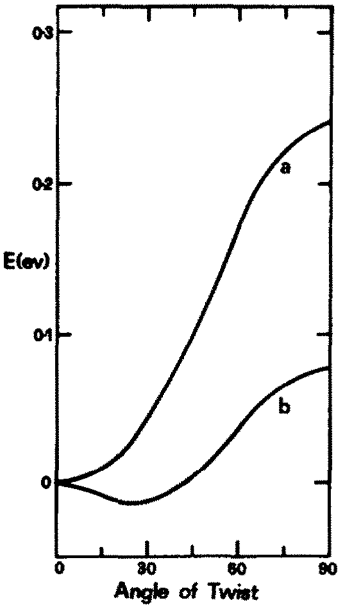

FIG 2. Extended Hückel energy *vs*. angle of twist for 2-phenylfuran (a) and 3-phenylfuran (b). The energy zero has been arbitrarily assigned to the planar conformation.

planar minimum near a twist angle of 30° and then rise markedly. A slightly distorted configuration shows thus some energetic advantage with respect to the all-planar geometry. (Incidentally, we observe that the curves established for these molecules resemble closely that determined by Hoffman *et al.*[9] for the related substance phenylcyclopentadienide anion).

The predictions for the pyrrole derivatives are consistent with IR evidence[10] which suggests that the steric interactions are small and are readily accommodated by a slight deviation from coplanarity. However, the configurations of the 2- and 3-phenyl pyrrole and furan are most likely not rigid, and the two rings probably oscillate in a limited angle interval about their equilibrium positions.

2- and 3-phenyl thiophene show similar curves (Fig. 3) with nearly equally deep minima at about 37°. Both of these molecules are then anticipated to have an equilibrium conformation twisted by about 37° from the planar geometry. It is interesting to note that also 2,2′- and 3,3,-bithienyl have been found both experimentally and theoretically to be non-planar.[11] The strikingly different situation observed for the thiophene derivatives compared with the related pyrroles and furans arises from stronger s–s and s–p interactions between the heteroatom and the neighbouring H atoms in the Ph ring. It should be noted that the calculations performed using also the 3d sulphur orbitals lead to ground-state geometries just as twisted as those established with the restricted basis s,p (Fig. 3).

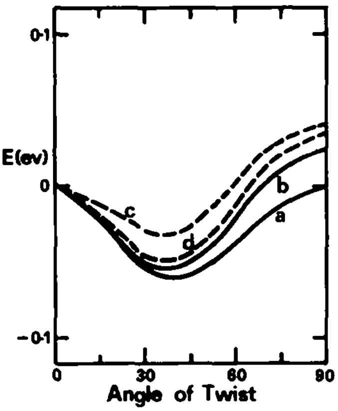

FIG 3. Extended Hückel energy *vs.* angle of twist for 2-phenylthiophene (a) and 3-phenylthiophene (b). The broken curves for 2-phenylthiophene (c) and 3-phenylthiophene (d) refer to the spd model for S. The energy zero has been arbitrarily assigned to the planar conformation.

Since the CNDO/2 method gives more reliable charge distributions than the EH theory, we have computed by this method the ground-state charge distribution of each molecule for the geometry corresponding to the "minimum" energy previously established. The parameters employed in these calculations have been taken from Ref. 12. Table 1 shows the net atomic charges, while Table 2 lists some important energy values.

TABLE 1. NET ATOMIC CHARGES

Atom	N-Phenyl pyrrole	2-Phenyl pyrrole	3-Phenyl pyrrole	2-Phenyl furan	3-Phenyl furan	2-Phenyl thiophene	3-Phenyl thiophene
X	−0·140	−0·235	−0·201	−0·339	−0·306	0·106	0·121
C-2	0·059	0·145	0·041	0·262	0·157	0·034	−0·078
C-3	−0·083	−0·108	−0·003	−0·115	−0·007	−0·096	0·017
C-4	−0·083	−0·078	−0·104	−0·077	−0·110	−0·053	−0·083
C-5	0·059	0·076	0·082	0·190	0·204	−0·052	−0·033
C-6	0·224	0·043	0·064	0·031	0·061	0·060	0·068
C-7	−0·079	−0·044	−0·049	−0·023	−0·046	−0·049	−0·048
C-8	0·006	−0·005	−0·005	−0·010	−0·004	−0·003	−0·006
C-9	−0·044	−0·027	−0·031	−0·021	−0·027	−0·030	−0·033
C-10	0·006	−0·005	−0·004	−0·007	−0·004	−0·003	−0·005
C-11	−0·079	−0·037	−0·044	−0·036	−0·043	−0·041	−0·046
H-N		0·161	0·155				
H-2	0·012		0·014		0·017		0·024
H-3	0·017	0·021		0·028		0·020	
H-4	0·017	0·018	0·021	0·025	0·028	0·018	0·021
H-5	0·012	0·010	0·011	0·012	0·014	0·021	0·021
H-7	0·024	0·010	0·010	0·025	0·012	0·012	0·012
H-8	0·016	0·012	0·010	0·014	0·013	0·013	0·011
H-9	0·016	0·013	0·010	0·014	0·013	0·013	0·012
H-10	0·016	0·013	0·010	0·013	0·013	0·013	0·011
H-11	0·024	0·017	0·013	0·014	0·015	0·017	0·014

Atom numbering is assumed to be as follows:

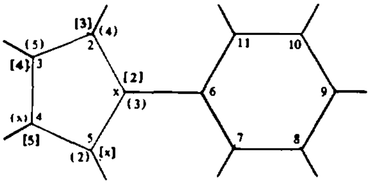

TABLE 2. SOME ENERGY CHARACTERISTICS

Molecule	HOMO (ev)	LEMO (ev)	$E_{elec.}$ (a.u.)	$E_{tot.}$ (a.u.)
N-Phenylpyrrole	−9·438	1·202	−277·6071	−26·6644
2-Phenylpyrrole	−8·879	0·842	−275·4459	−27·2454
3-Phenylpyrrole	−9·095	1·260	−274·1645	−27·5263
2-Phenylfuran	−9·001	0·648	−280·6330	−31·9405
3-Phenylfuran	−9·320	0·993	−278·7390	−32·1370
2-Phenylthiophene	−9·063	0·844	−268·8612	−29·3211
3-Phenylthiophene	−8·935	1·146	−269·3828	−29·3137

The overall charge distribution in a molecule is reflected in some measure by the dipole moment, which has been evaluated by the Pople-Segal approach.[13] The dipole moment is calculated to be 1·79 D for N-phenylpyrrole (exp. 1·32 D,[7] 1·62 D),[14] 0·53 D for 2-phenylthiophene (exp. 0·58 D,[15] 0·18 D),[16] and 0·89 D for 3-phenylthiophene (exp. 0·49 D,[15] 0·80 D),[16] in good agreement with the experimentally determined values. Finally, the dipole moment is predicted to be 2·06 D for 2-phenylpyrrole, 2·55 D for 3-phenylpyrrole, 0·64 D for 2-phenylfuran, and 0·71 D for 3-phenylfuran.

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