Conformational Behaviour of Phenylpyrroles – a Semiempirical Molecular Orbital Study

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Equilibrium twist angles and rotational barriers for the three isomeric phenylpyrroles were calculated by means of MNDO and AM1. In each case MNDO incorrectly predicts the perpendicular conformation as the most stable one. In agreement with experimental evidence AM1 predicts only slight deviations from planarity and very low 0°-barriers (1-phenylpyrrole: $\theta = 28°$, $E = 1.6$ kJ mol^{-1}; 2-phenylpyrrole: $\theta = 27°$, $E = 0.8$ kJ mol^{-1}; 3-phenylpyrrole: $\theta = 19°$, $E = 0.2$ kJ mol^{-1}). The reasons for the complete failure of MNDO are analyzed by partitioning the total energy into one- and two-center terms. The most significant improvement of AM1 over MNDO is found to be the much better description of repulsive interactions between non-bonded atoms. Possible further improvements of AM1 are briefly discussed.

Introduction

Conformational problems are frequently encountered in the interpretation of the electronic absorption spectra of organic compounds [1]. For instance, in an attempt to rationalize the ultraviolet spectra of benzopyrroles and -dipyrroles, e. g. **1**, the conformation of the phenyl groups was of interest [2]. A similar problem is encountered in an analysis currently under way of the electron spectroscopic properties of pyrazolone dyes, e. g. **2** and **3**. Further interest in ground state torsional potentials stems from the fact that among other things the equilibrium twist angle in the ground state has been recognized as an important factor in determining the kinetics for TICT (twisted intramolecular charge transfer) state formation [3]. Unfortunately, standard semiempirical methods of quantum chemistry, e. g. CNDO/2 [4], INDO [5], MINDO/3 [6] and MNDO [7], do not give even qualitatively correct potential functions for the rotation about essential single bonds in conjugated compounds, typically favouring perpendicular arrangements [8]. In the case of CNDO/2 as well as INDO-based methods (INDO, MINDO/3) the central inadequacy has been attributed to the oversimplified treatment of the two-center exchange interaction [8]. To overcome the shortcomings of these methods an extension of the formalism at least to the NDDO level of approximation has been suggested [8]. MNDO although based on the NDDO approximation still suffers from the very same shortcomings as its predecessor MINDO/3, probably due to an overestimation of non-bonded repulsions [9, 10]. Recently, Dewar et al. proposed a new semiempirical method (AM1) which has been claimed to largely correct the errors associated with MNDO [10]. Since – as has been stated above – conformational problems are frequently encountered in chemistry a detailed knowledge of the applicability and limitations of semiempirical methods seems to be quite necessary. We therefore thought it worthwhile to study the performance of AM1 with respect to conformational problems. Due to our interest in compounds of type **1–3** we chose for this purpose the three isomeric phenylpyrroles **4–6** as simple model compounds.

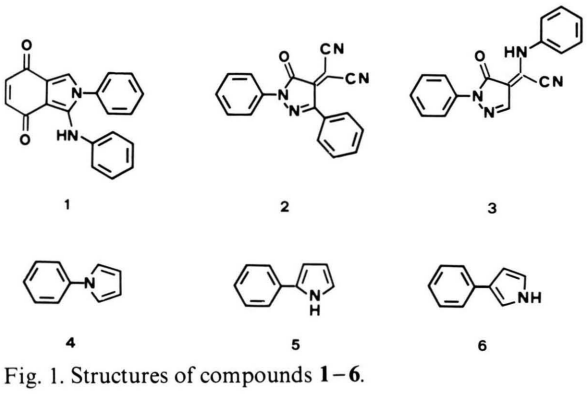

Fig. 1. Structures of compounds **1–6**.

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Calculational Details

All calculations were performed with the AMPAC program package [11] using the MNDO or AM1 option. The torsional potential was computed in steps of 30° with complete optimization of all remaining geometrical parameters and fitted to a six-term Fourier expansion [12]:

$$\delta E = E(\theta) - E(0°) = 1/2 \sum_j V_j[1 - \cos(j\theta)]. \quad (1)$$

Due to symmetry requirements ($E(0°) = E(180°)$) only even terms contribute to this expansion. In order to test the reliability of the torsional potential obtained in this way a further calculation at $\theta = 45°$ was performed. To assess the main factors responsible for the conformational behaviour of the three isomeric phenylpyrroles the energy partitioning technique into one- (E_A) and two-center (E_{AB}) contributions was employed [13]:

$$E = E_A + E_{AB}. \quad (2)$$

The two-center terms E_{AB} may be further decomposed into a resonance term E_{AB}^R and an electrostatic contribution E_{AB}^Q [13]. Alternatively, E_{AB} may be represented as sum of terms arising from chemically bonded (E_{AB}^b) and non-bonded atoms (E_{AB}^{nb}), respectively [14, 15]. This latter decomposition seems particularly useful for our purpose since the main difference between AM1 and MNDO is a modified representation of non-bonded interactions in AM1 [10].

Results

The results (equilibrium twist angles θ, rotational barriers and coefficients of the Fourier expansion (1)) are collected in Table 1.

Experimental evidence [3, 16–18] points to a planar or at least approximately planar equilibrium conformation of compounds **4–6**, although with a rather large distribution function [3]. It is clear from the data of Table 1 that MNDO, which consistently predicts the perpendicular arrangement of the two rings as the most stable conformation is not suitable for conformational studies. In sharp contrast the AM1 results are in excellent agreement with the experimental findings. Since the calculated barriers to planarity are very low (in the order of magnitude of thermal energies, see Table 1) the phenylpyrroles may be viewed as effectively planar compounds. Extended Hückel calculations on 1-phenylpyrrole led to an equilibrium twist angle of 40° [19] and 50° [20], respectively, as well as much larger barriers to planarity (~ 11 kJ mol^{-1} [19], 16.7 kJ mol^{-1} [20]). It is interesting to note that the 90°-barriers found in these studies are smaller than the 0°-barriers (~ 9 kJ mol^{-1} [19], 4.5 kJ mol^{-1} [20]), which clearly is in contradiction to experimental evidence. For 2- and 3-phenylpyrrole the potential curves obtained by the EHT method [19] resemble much closer those calculated by AM1. Figure 2 shows the torsional potentials obtained from (1). As can be seen, the additional point calculated at $\theta = 45°$ perfectly lies on these curves thus corrobating the adequacy of using (1).

In order to analyze this distinctly different performance of MNDO vs. AM1 with respect to torsional isomerism some pertinent results of the energy partitioning technique are listed in Table 2. The entries collected there are the differences of the various energy components between perpendicular and planar conformations. Thus a negative sign indicates a stabilization of the 90° conformer relative to the planar one.

Based on these results the following conclusions can be drawn:

Table 1. Equilibrium twist angles, rotational barriers and Fourier coefficients [kJ mol^{-1}].

	1-phenylpyrrole		2-phenylpyrrole		3-phenylpyrrole	
	MNDO	AM1	MNDO	AM1	MNDO	AM1
θ	90°	28°	90°	27°	90°	19°
0°-barrier	15.4	1.6	11.8	0.8	9.9	0.2
90°-barrier	0.0	8.3	0.0	6.1	0.0	6.8
V_2	−14.8	8.0	−11.6	6.0	−9.5	7.2
V_4	−4.7	−3.1	−2.8	−2.2	−2.9	−1.4
V_6	−0.6	−1.2	−0.2	−0.7	−0.4	−0.6

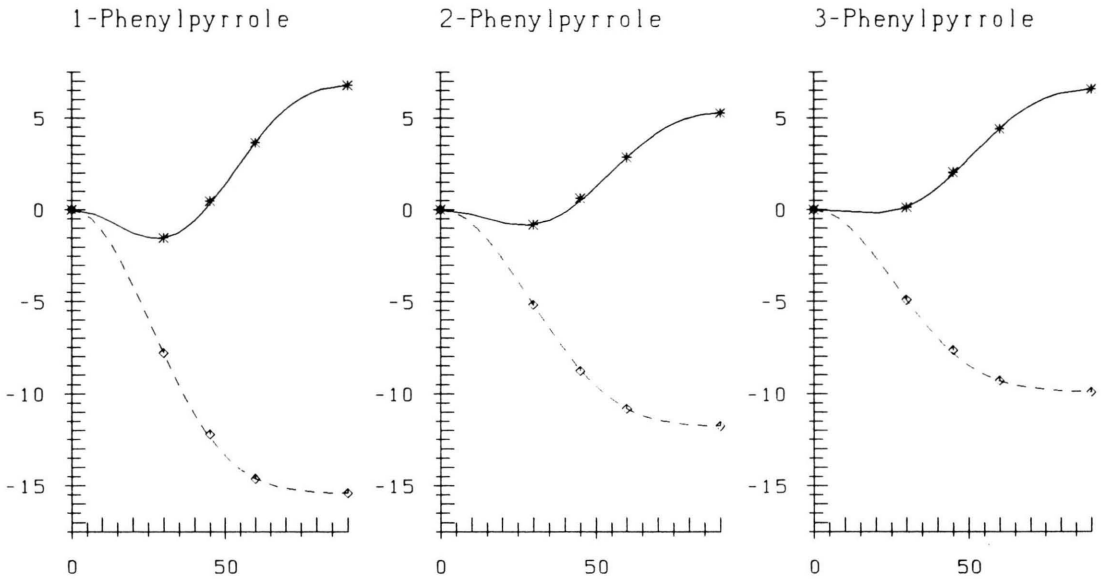

Fig. 2. Torsional potential function [kJ mol^{-1}] for compounds **4**–**6** obtained from (1) (solid lines: AM1; dashed lines: MNDO).

Table 2. Differences of the various energy components [kJ mol^{-1}] between perpendicular and planar conformations.

	1-phenylpyrrole		2-phenylpyrrole		3-phenylpyrrole	
	MNDO	AM1	MNDO	AM1	MNDO	AM1
E_A	−22.4	−31.3	−1.9	−10.8	2.1	−9.3
E_{AB}	7.0	38.1	−9.9	16.1	−12.0	15.9
E_{AB}^{b}	30.0	41.9	5.2	20.8	4.0	21.6
E_{AB}^{nb}	−23.2	−3.9	−15.4	−4.8	−16.4	−5.8
E_{HH}^{nb}	−8.1	−1.4	−5.1	−1.0	−4.9	−1.2

i) In the case of AM1 the one-center contribution E_A to the total energy strongly favours perpendicular conformations, especially for 1-phenylpyrrole. A similar result is obtained for this compound using MNDO, whereas for 2- and 3-phenylpyrrole E_A (MNDO) is roughly constant.

ii) The main reason for the failure of MNDO can be traced back to an inadequate handling of the two-center energies: In AM1 the decrease of the E_A's is more than compensated by a drastic increase of E_{AB} thus favouring planar or nearly planar structures. In sharp contrast MNDO yields only an insignificant increase of E_{AB} in the case of compound **4**, which cannot compensate the much larger decrease of the one-center energy. For compounds **5** and **6** MNDO even predicts a decrease of E_{AB} thus strongly favouring the perpendicular conformation.

iii) The decomposition of E_{AB} into bonding (E_{AB}^{b}) and non-bonding E_{AB}^{nb} contributions clearly shows that MNDO drastically overestimates the repulsion between non-bonded atoms. In AM1 these interactions are reduced to about 30% of the MNDO values. In addition AM1 also seems to give a more realistic description of bonded interactions (Table 2).

iv) Finally, the data in Table 2 indicate that approximately 30% of the non-bonded repulsion are contributed by the hydrogen atoms in the ortho-positions (E_{HH}^{nb} in Table 2). Again in AM1 this energy term is reduced to at least 30% as compared to MNDO.

Conclusions

From the above discussion it seems clear that AM1 represents a very real improvement over MNDO with respect to conformational problems. We are thus confident that this method will also give reliable results for the compounds of type **1–3**. However, although information concerning calculated rotational barrier heights is too scarce for definite conclusions to be drawn it seems that AM1 yields values which are still much too low (e.g. for formamide the calculated barrier is approximately one half of the experimental value [10]). The analysis in terms of the various energy components presented above thus should be useful for further improvements of this method, e.g. a more realistic description of the one-center energies which apparently drop too drastically in going from the planar to the perpendicular conformation.

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