

CONFORMATIONAL ENERGIES OF AROMATIC POLYAMIDES

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Abstract—PCILO conformational calculations have been made on several model compounds of aromatic polyamides. The calculated structures can be compared with the X-Ray crystallographic analyses and related to the physical properties of these polymers. Poly-*p*-phenylene terephthalamide appears as a more flexible polymer than poly-*p*-benzamide.

INTRODUCTION

X-Ray crystal structures of various aromatic polyamides have been investigated by several authors [1–6]. Poly-*p*-benzamide (PPBA) and poly-*p*-phenylene-terephthalamide (PPPTA) are of particular interest because of their unique physical properties, such as the extremely high modulus of fibres based on them, and their liquid-crystalline behaviour in solution. Moreover it has been shown that the main factors determining the equilibrium flexibility of these molecules can be discussed in terms of conformational considerations [7]. A brief empirical conformational energy calculation has already been performed on PPPTA by Tadokoro [5] but it appeared interest-

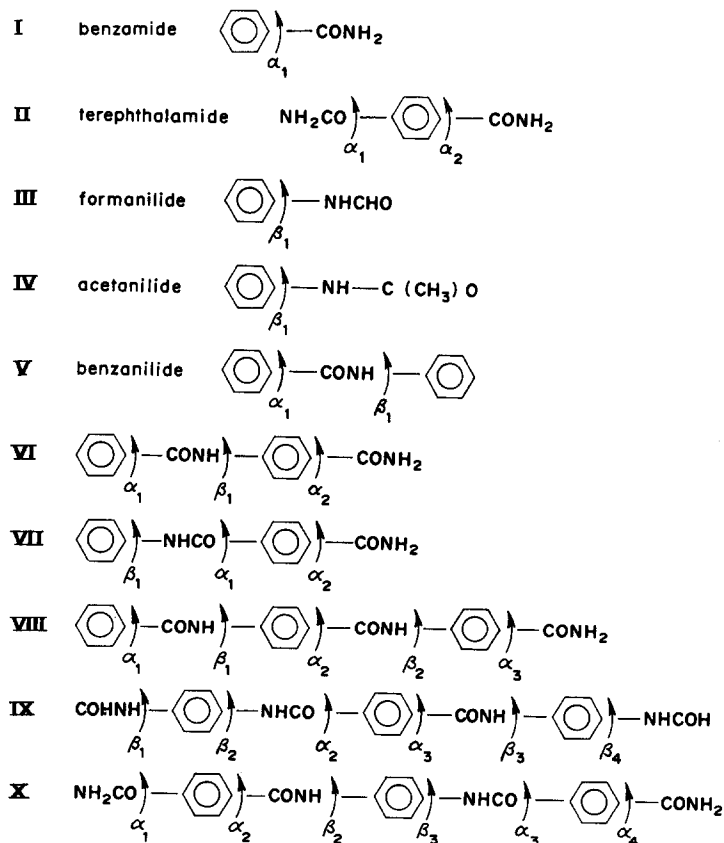
ing to gain a much more precise insight into the conformational energies of model compounds of aromatic polyamides. Therefore this paper deals with results obtained from the PCILO (Perturbative Configuration Interaction using Localized Orbitals) program [8]. This method accounts for both steric and conjugative effects, and has already been used successfully in conformational studies of nicotinamides [9], nucleic acids and a number of amino acid residues of proteins [10].

DESCRIPTION OF THE CALCULATIONS

The calculation of the conformational energies of model compounds of aromatic polyamides is accomplished by employing the PCILO method [8]*.

The molecules under study are listed below:

* The PCILO program was provided by Dr. H. Berthod, of the Institut de Biologie Physico-Chimique, Paris.



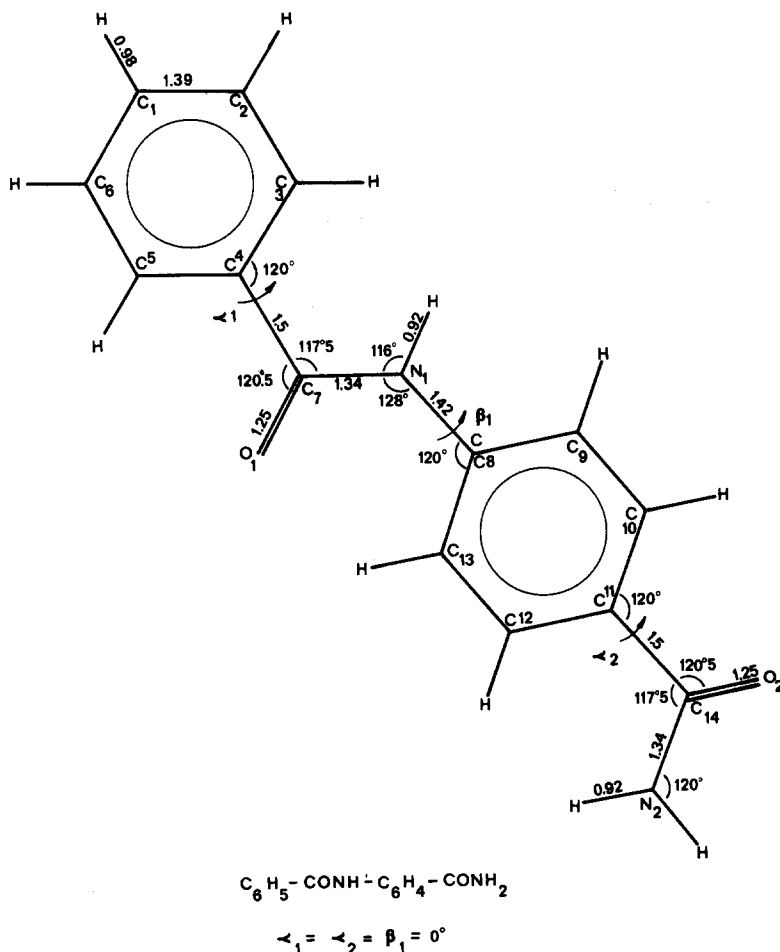


Fig. 1. Internal rotation angles, bond angles and bond lengths of $C_6H_5-CONH-C_6H_4-CONH_2$ (VI).

Figure 1 presents as an example the drawing of molecule VI. The internal rotation angles investigated are α_i and β_i , defining the orientation of the i^{th} amide group with respect to the two adjacent rings. The values $\alpha_i = 0^\circ$ and $\beta_i = 0^\circ$ correspond to the planar configuration. For molecules with two or more amide groups, α_i and β_i are taken as zero when the C=O groups are pointing alternatively up and down, as shown on Fig. 1.

The geometrical input data are given in Fig. 1. They are taken from crystallographic measurements and studies of Blake and Small [11], Mornon [12], Tadokoro [4] and Northolt [3]. Mean values of 1.39 Å and 120° are adopted for the benzene ring geometry, and for the $\langle C_{AR}C_{AR}C_{AMIDE} \rangle$ ($\langle C_3C_4C_7 \rangle$) angle. The aliphatic C-CH₃ and C-H bonds of acetanilide and formanilide are taken as 1.54 and 0.95 Å, and the C-H length of a methyl group as 1.1 Å. The carboamide group C₄C₇ON is assumed to be planar, in quite good agreement with X-ray data both on benzamide [11] and acetanilide [13]. We will check the validity of this assumption in the case of benzamide. Only the trans-structure of the amide groups is considered because Tsvetkov [7] has shown that such a "crankshaft"-like conformation is a structural property of aromatic polyamides with phenyl rings included in the chain in the para position.

The computations have been carried out in 30° increments. For the smallest compounds (I and III), the low energy conformers were refined by stepping each rotation angle in 10° increments about the crudely generated structures.

RESULTS AND DISCUSSION

1. Benzamide (I)

The conformational energy curve for the amide group rotation about the C₄-C₇ bond is shown on Fig. 2. It shows a minimum for $\alpha_1 \approx 20^\circ$. The departure from coplanarity between the ring and the side-chain is in good agreement with the X-ray crystal data which give $\alpha_1 = 24^\circ$ [11] and 26° [14] and so can be assigned to purely intramolecular effects as suggested by Blake and Small [11]. These results are also very similar to the PCILO calculations of Coubeils, Pullman and Courrière on nicotinamide [9], in striking agreement with the X-ray crystal structure [15,16] of this compound that closely resembles benzamide. The conformational energy of I is very low in the range 0° - 30° , which predicts a high freedom of oscillation between these two limits. The energy barrier for the amide group rotation about the C₄-C₇ bond is 2.1 kcal/mole, which can be compared with the 2.6 kcal/mole calculated for nicotina-

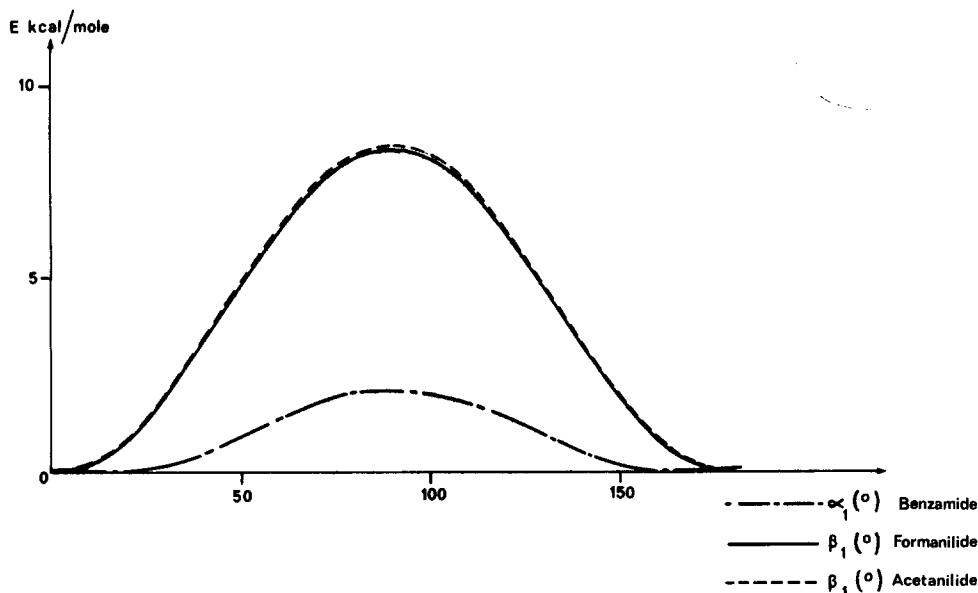


Fig. 2. The conformational energy for the rotation of: the CO—NH₂ group of benzamide about the C₄—C₇ bond; the NH—CO group in formanilide and acetanilide.

amide [9], and is not very far from the 4.7 kcal/mole measured for gaseous benzaldehyde [17]. Therefore the choice of the PCILO program for such molecules appears more satisfactory than those of PPP and CNDO/2 methods previously used for benzamide [18].

The conformational energy for the amide group rotation about the C₇—N bond has been calculated in the most stable ($\alpha_1 = 20^\circ$) conformation of benzamide. The corresponding energy barrier is 15.6 kcal/mole. The experimental value for formamide lies in the range 17–21 kcal/mole. It is high enough to permit assumption of planarity of the amide group in trans conformation for the further calculations. However, it should be noted that small deformations of 5° to 10° can occur, as suggested by Tsvetkov [7].

2. Terephthalamide (II)

The conformational energy contour for the two amide group rotations is presented in Fig. 3. It does not show any important difference from benzamide. The absolute minimum is obtained for $\alpha_1 = \alpha_2 = 0^\circ$.

However, as the conformational energy remains very weak in the range 0°–30° for each of the two angles, the preferred conformation must be considered as located between these two values, again in good agreement with the X-ray data that give $\alpha_1 = \alpha_2 = 23^\circ$ [19].

3. Formanilide (III) and Acetanilide (IV)

The conformational energy curves for the NH—C=O group rotation about the C_{AR}—N bond in the endo forms of III and IV are drawn in Fig. 2. As noted for the previous molecule, the absolute minimum is reached for 0° but the accuracy of the calculation does not allow us to localize the preferred conformation between 0° and 20° more precisely. From proton magnetic resonance measurements, Rae [20] has shown that the formamide group of formanilide in dimethylsulphoxide solution lies in the ring plane. The refined crystal structure of acetanilide due to Brown [13] gives $\beta = 17^\circ 6'$.

The energy barrier for this internal rotation is over 8 kcal/mole for both compounds, which is much

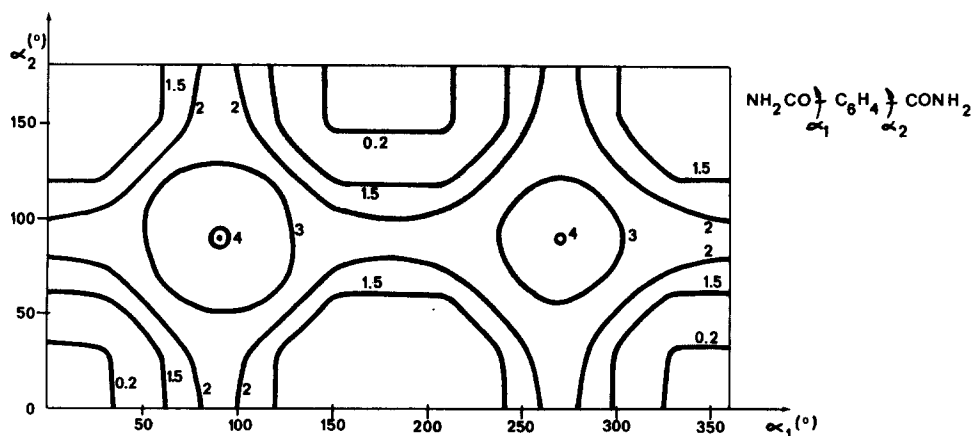


Fig. 3. The conformational energy of terephthalamide for the two amide group rotations α_1 and α_2 .

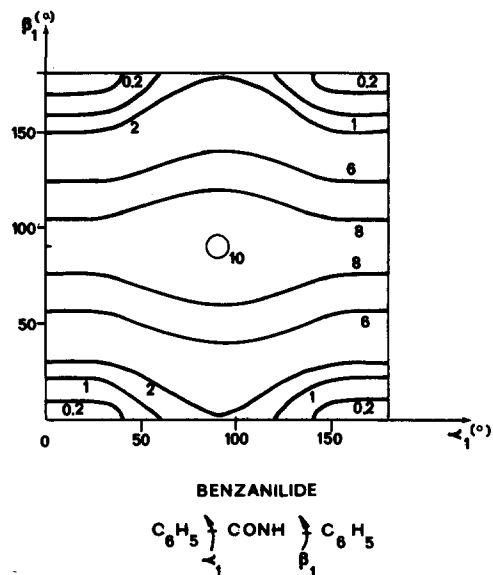


Fig. 4. The conformational energy contour of benzanilide for the two internal rotation angles α_1 and β_1 .

higher than the corresponding barrier calculated for benzamide and terephthalamide. Therefore, the main difference between molecules I and II on the one hand, and III and IV on the other, appears to be their rigidity.

4. Model compounds of poly-p-benzamide

The conformational energy maps for benzanilide (V) and molecules VI and VIII are given on Figs 4, 5 and 6. All three molecules present the same characteristics as those calculated for compounds I to IV. The α rotation angle of the phenyl ring with respect to any adjacent C=O of a CONH group is about 20° – 30° and the freedom of oscillation is very high in the range 0° – 30° . The energy barrier for each α rotation is 2 kcal/mole, equal to that obtained for benzamide. The behaviour of the CONH₂ end-group of VI is exactly similar to that of terephthalamide. Analogy with formanilide shows that the β rotation angle of the ring with respect to any adjacent NH of a NHCO group lies in the range 0° – 20° and the corresponding barrier is 9.0 kcal/mole. Both results on α and β rotations may lead to a mean angle of 20° between the ring and the amide planes, in satisfactory agreement with the crystallographic data of Tadokoro on PPBA [1]. Moreover the fibre identity period determined from our equilibrium parameters is 12.8 Å, equal to those calculated (12.8 Å) and measured (12.9 Å) by Tadokoro [1].

In molecule VIII, the conformation in which the C=O groups alternately point up and down and that in which they all point in the same direction are nearly isoenergetic (Fig. 6). Therefore these calculations do not allow choice between the polymer in which all par rings are approximately parallel, or the regularly bent one suggested by Tsvetkov [7]. In this

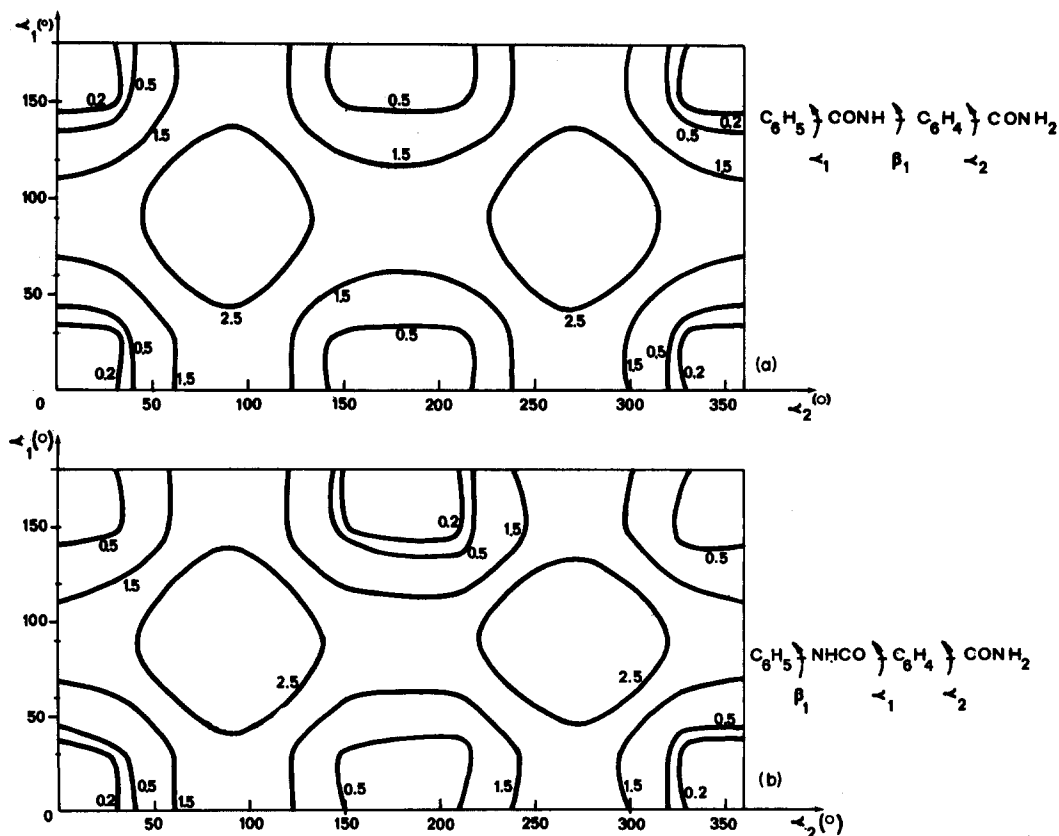


Fig. 5. The conformational energies of VI (Fig. 5a) and VII (Fig. 5b) for the two internal rotation angles α_1 and α_2 , β_1 being taken as 0° .

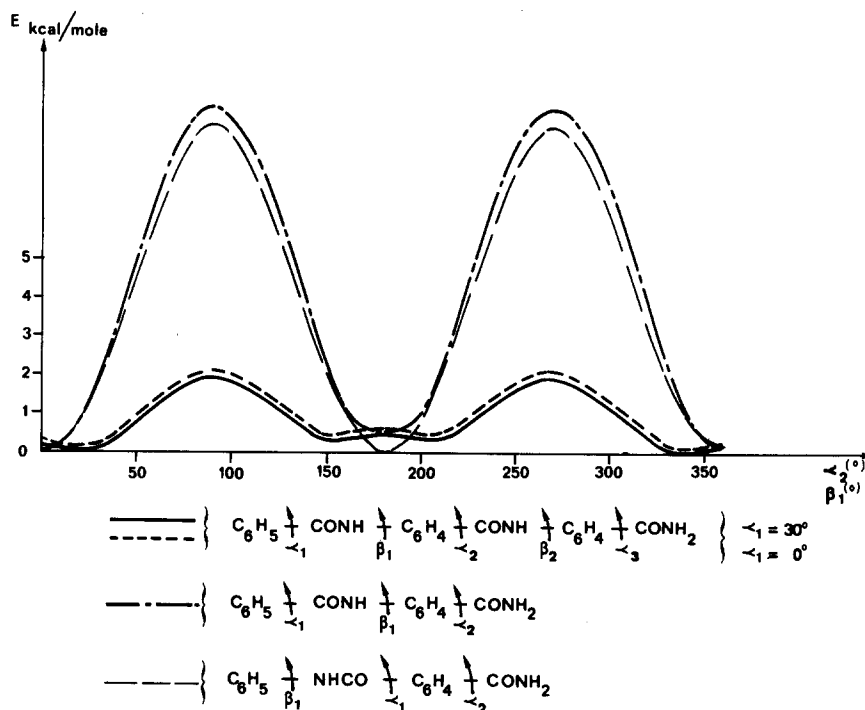


Fig. 6. The conformational energy of: VI, as a function of β_1 (with $\alpha_1 = 30^\circ$, $\alpha_2 = 0^\circ$); VII, as a function of β_1 (with $\alpha_1 = 30^\circ$, $\alpha_2 = 0^\circ$); VIII, as a function of α_2 for $\alpha_1 = 0^\circ$ and $\alpha_1 = 30^\circ$, β_1 , β_2 and α_3 being taken as 0° .

latter case, it must be noted that the use of crystallographic angles of $117^\circ 5'$ and 128° for the $\langle C_{AR}C_{AMIDE}N_{AMIDE} \rangle$ and $\langle C_{AMIDE}N_{AMIDE}C_{AR} \rangle$ angles causes a chain curving of $\Delta\theta = 10^\circ 5'$, in the limits of the possible values of $\Delta\theta = 6^\circ - 12^\circ$ according to the literature [7, 21].

These PCILO calculations on PPBA model molecules lead to a description of the polymer chain very similar to that given by Tsvetkov [7] in which rings with relatively free rotation and amide groups with a fixed coplanar trans-structure alternate regularly. We can add that the oscillations of the phenyl ring have considerable freedom in the range $\alpha = \beta = 0^\circ - 20^\circ$ or 30° , but that the complete rotation is somewhat hindered by the height of the energy barrier about the $C_{AR}-N$ bond. It has already been noted [7] that such a structure accounts for the physical properties of PPBA, particularly for its capability of giving mesomorphic solutions, and for the properties of very high modulus fibres based on it.

5. Model compounds of poly-p-phenylene terephthalamide

The conformational contours of the model molecules of PPPTA (V, VII, IX) are shown on Figs 4, 5b, 6 and 7. The energy barrier for the central phenyl ring of X about the C—N adjacent bonds is 8.7 kcal/mole. The conformational characteristics of V, VII, IX and X are the same as those pointed out for the various previous compounds. From these results, we conclude that the angle of the terephthalic segment with respect to the phenyl ring is about 30° , in good agreement with the crystallographic analysis of PPPTA performed by Northolt [3]. The rotation angle between the paraphenylenediamine and the ring

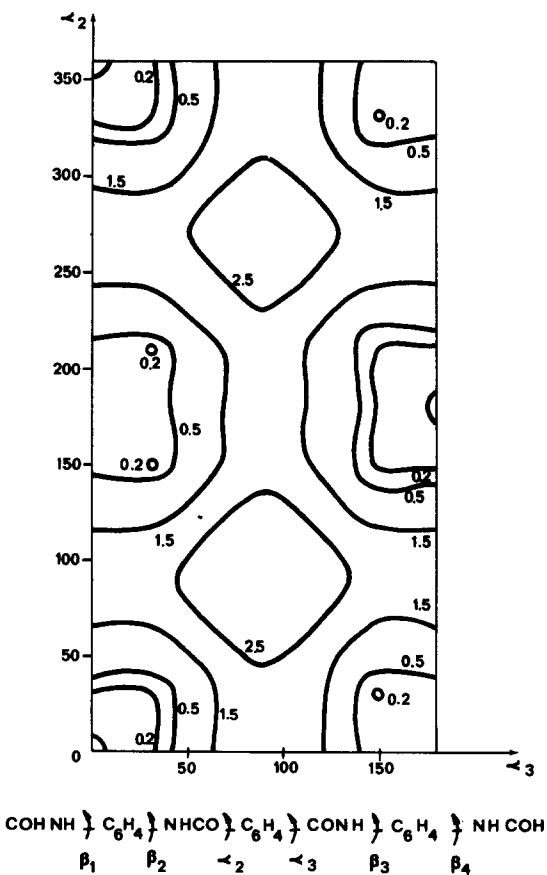


Fig. 7. The conformational energy contours of IX. β_1 , β_2 , β_3 , β_4 are taken as 0° .

planes lies in the range 0° – 20° : it is smaller than the value (38°) given by Northolt [3] but in better agreement with PMR and X-ray data on small model compounds **III** and **IV** [20, 13]. The energy barrier about the C_{AR} —N bond is relatively high (9 kcal/mole) but rotation about the C_{AR} — C_{AMIDE} bond appears much easier (2 kcal/mole). This last point agrees with the well-known experimental fact that PPPTA is a more flexible polymer than PPBA.

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REFERENCES

1. R. K. Hasegawa, Y. Chatani and H. Tadokoro, *Reports on progress in Polymer Physics in Japan* **16**, 217 (1973).
2. M. G. Northolt and J. J. Van Aartsen, *J. Polym. Sci., Polym. Lett. Ed.* **11**, 333 (1973).
3. M. G. Northolt, *Europ. Polym. J.* **10**, 799 (1974).
4. H. Kakida, Y. Chatani and H. Tadokoro, *J. Polym. Sci. Polym. Phys. Ed.* **14**, 427 (1976).
5. K. Tashiro, M. Kobayashi and H. Tadokoro, *Macromolecules* **10**, 413 (1977).
6. K. Yabuki, H. Ito and T. Ota, *Sen-I Gakkaishi* **31**, 524 (1975).
7. V. N. Tsvetkov, *Europ. Polym. J.* **12**, 867 (1976).
8. S. Diner, J. P. Malrieu, F. Jordan and M. Gilbert, *Theoret. Chim. Acta* **15**, 100 (1969).
9. J. L. Coubeils, B. Pullman and Ph. Courrière, *Biochem. Biophys. Res. Commun.* **44**, 1131 (1971).
10. *Quantum Mechanics of Molecular Conformations*. (Edited by B. Pullman) Ch. 4. Wiley-Interscience, New York (1975).
11. C. C. F. Blake and R. W. H. Small, *Acta Crystallogr. B* **28**, 2201 (1972).
12. J. P. Mornon, *Acta Crystallogr. B* **26**, 1985 (1970).
13. C. J. Brown, *Acta Crystallogr.* **21**, 442 (1966).
14. B. R. Penfold and J. C. B. White, *Acta Crystallogr.* **12**, 130 (1959).
15. W. B. Wright and G. S. King, *Acta Crystallogr.* **7**, 283 (1954).
16. I. L. Karle, *Acta Crystallogr.* **14**, 497 (1961).
17. W. G. Fateley, R. K. Harris, F. A. Miller and R. E. Witkowski, *Spectrochim. Acta* **21**, 231 (1965).
18. P. N. Skancke and I. Aanesland, *Acta Chem. Scand.* **26**, 2614 (1972).
19. R. E. Cobbleddick and R. W. H. Small, *Acta Crystallogr. B* **28**, 2893 (1972).
20. I. D. Rae, *Can. J. Chem.* **44**, 1334 (1966).
21. U. Shmueli, W. Traub and K. Rosenheck, *J. Polym. Sci.* **7**, A2, 515 (1969).

Résumé—Des calculs conformationnels de type PCILO ont été réalisés sur plusieurs molécules modèles de polyamides aromatiques. Les résultats obtenus sont très comparables à ceux fournis par les études cristallographiques, et peuvent être reliés aux propriétés physiques de ces polymères. Le poly-*p*-phénylène téréphthalamide apparaît comme une molécule plus flexible que le poly-*p*-benzamide.