Structural Geometry and Torsional Potentials in *p*-Phenylene Polyamides and Polyesters

J. P. Hummel and P. J. Flory*

IBM Research Laboratory, San Jose, California 95193. *Received December 21, 1979*

ABSTRACT: Structural data from X-ray crystallographic investigations on aromatic amides and esters are examined for the purpose of deducing bond lengths and bond angles appropriate for poly(*p*-benzamide), poly(*p*-phenyleneterephthalamide), and the corresponding polyesters. Conformational energies have been calculated for acetanilide (AA), *N*-methylbenzamide (NMB), phenyl acetate (PA), and methyl benzoate (MB) as functions of torsion angles about the phenylene axes. An empirical force field (6-exp type) supplemented by terms for frame distortion and electron delocalization was used for this purpose. Bond angles and bond lengths were adjusted to values that minimize the total energy at each value of the torsion angle. Delocalization energies that optimize agreement of the torsional minima with torsion angles observed in the crystals of the four compounds and their analogues are 7 kcal mol^{-1} for AA and NMB and ca. 3 kcal mol^{-1} for PA. Torsional energies calculated for these molecules exhibit maxima at coplanarity of the amide or ester group with phenyl, owing to steric repulsions involving ortho hydrogens; they exhibit minima near ±30°, ±30°, and ±55°, respectively. Steric interactions are small in MB and the torsional energy is minimal in the coplanar form for any value of the delocalization energy greater than 3 kcal mol^{-1}. Crystallographic results confirm the coplanar form as the stable conformation. The empirical torsional energies are compared with ab initio molecular orbital calculations.

Aromatic polyamides and polyesters in which phenylene residues are linked directly by amide or ester groups constitute a class of polymers having unusual configurational characteristics.[2-5] The most prominent examples are poly(*p*-benzamide), poly(*p*-phenyleneterephthalamide),[2,3] and the corresponding polyesters.[4,5] Regular planar conformations of these polymers are shown in Figure 1. The overwhelming preference of the amide and the ester groups for the planar, trans configurations, and the large torsional potentials opposing rotations about the amide and ester bonds, render the axes of successive phenylene groups effectively coplanar. The angle δ between them is only 7–10°; it is determined by the difference between the skeletal bond angles at carbonyl and at nitrogen, or at oxygen in the esters. The directions of successive units consequently are strongly correlated, and this correlation is perpetuated over many units. The chains therefore tend to be highly extended.

Rotations about the phenylene axes, denoted by the torsions ϕ and ψ defined in Figure 1, admit of irregularity transverse to these axes.[6] The torsional potentials affecting these rotations necessarily are symmetric with respect to the conformations in which the phenylene ring and the adjacent amide or ester group are coplanar. Moreover, alteration of ϕ or ψ by 180° entails, at most, only a small change in the potential. These features of the torsional potentials, implicit in the structures of these molecules, assure a diversity of directions accessible to the projections of the amide or ester bond in the plane normal to the phenylene axis. Torsional rotations therefore impart randomness transverse to the chain backbone. Moreover, in conjunction with the departures of the phenylene axes from parallelity, they allow very long chains to acquire the characteristics of three-dimensional random coils, as detailed more fully in the following paper.[7]

It will be evident that the spacio-configurational properties of the chains considered are sensitively dependent on their structural geometry and on the potentials affecting torsional rotations. In this paper we examine available structural data, relying in large measure on the results of X-ray crystallographic investigations on model compounds reported recently by Harkema and Gaymans,[8] by Adams, Fratini, and Wiff,[9] by Harkema, Gaymans, van Hummel, and Zylberlicht,[10] and by Adams and Morsi.[11] Second, we have attempted to formulate approximate torsional potentials that are consistent with indications of experimental results on related low molecular compounds. For this purpose, we have relied mainly on empirical methods for estimating the interactions between nonbonded atoms and the strain energies resulting from distortions of the molecular frame. These calculations have been carried out with full relaxation of bond lengths and bond angles in each conformation defined by ϕ or ψ. Included in the total conformational energy is a contribution from electron delocalization. Its magnitude is adjusted to render the conformation of lowest energy compatible with the conformations of model compounds in the crystalline state as revealed by X-ray diffraction, including especially the results of the investigations cited above.

Lauprêtre and Monnerie[12] have carried out molecular orbital (PCILO) calculations on aromatic amides from which they obtain the energy as a function of the torsion angles ϕ and ψ. Their results are compared with those we have obtained with the use of empirical force field methods. We also cite preliminary ab initio molecular orbital calculations[13] that compare favorably in most respects with the empirical calculations and with inferences from structure.

The structural parameters and torsional potentials deduced here are applied in the following paper[7] to the calculations of persistence vectors and of higher moments of the chain vector **r**.

Skeletal Bond Angles and Preferred Conformations According to Crystallographic Results on Model Compounds

Crystallographic data on bond angles τ_1 and τ_2 and on torsion angles ϕ and ψ (see Figure 1) are listed in Tables I and II for aromatic amides and esters, respectively. The torsion angles are measured from the conformation in which the amide or ester group is coplanar with the adjoining phenylene ring.

The first two compounds listed in Table I, namely, *N*,*N*′-*p*-phenylenebenzamide and *N*,*N*′-diphenylterephthalamide, are most closely analogous to the *p*-phenyl polyamides. Two crystalline forms of the former compound have been investigated.[8,9] Values of the bond angle τ_1 at the carbonyl carbon in these compounds are about 2–3° smaller than those for the various benzamides whose crystal structures have been determined. Similarly, τ_2 for the prototype compounds is about 3° lower than those for

Table I
Bond and Torsion Angles in Crystalline Aromatic Amides

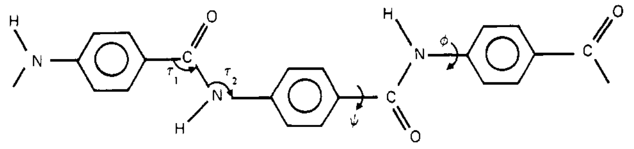
compd	τ_1, deg	τ_2, deg	ϕ, deg	ψ, deg	ref
N,N-p-phenylenebenzamide (monoclinic)	115.0	124.9	35.9	29.1	a
N,N-p-phenylenebenzamide (orthohombic)	116.1	122.0	56.3	22.7	b
N,N-diphenylterephthalamide	115.5	126.8	30.4	30.6	c
benzamide	117.5			24.6	d
terephthalamide	117.7			23.0	e
N-methylbenzamide	119.1			28.7	f
N-hydroxybenzamide	118.1			24.4	g
exo-N-(2-norbornyl)benzamide	118.1			25.4	h
acetanilide		127.6	17.6		i
p-bromoacetanilide		128.9	5.8		j
p-chloroacetanilide		127.0	5.0		k
p-hydroxyacetanilide (orthohombic)		129.8	17.7		l
p-hydroxyacetanilide (monoclinic)		128.3	21.2		m
3,4-dichloroisobutyranilide		126.5	26.6		n
4-chlorodipropylacetanilide		126.2	39.8		o

[a] See ref 8. [b] See ref 9. [c] See ref 10. [d] C. C. F. Blake and R. W. H. Small, *Acta Crystallogr., Sect. B*, **28**, 2201 (1972). [e] R. E. Cobbledick and R. W. H. Small, *ibid.*, **28**, 2893 (1972). [f] S. Orii, T. Nakamura, Y. Takaki, Y. Sasada, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **36**, 788 (1963). [g] Y. Katsube, Y. Sasada, and M. Kakudo, *ibid.*, **39**, 2576 (1966). [h] M. G. Newton, N. S. Pantaleo, S. Kirbany, and N. L. Allinger, *J. Am. Chem. Soc.*, **100**, 2176 (1978). [i] C. J. Brown, *Acta Crystallogr.*, **21**, 422 (1966). [j] G. D. Andreetti, L. Cavalca, P. Domiano, and A. Musatti, *Acta Crystallogr., Sect. B*, **24**, 1195 (1968). [k] E. Subramanian, *Z. Kristallogr., Kristallgeom., Kristallphys.*, **123**, 222 (1966). [l] M. Haisa, S. K. Ashino, and H. Maeda, *Acta Crystallogr., Sect. B*, **30**, 2510 (1974). [m] M. Haisa, S. K. Ashino, R. Kawai, and H. Maeda, *ibid.*, **32**, 1283 (1976). [n] G. Precigoux, B. Busetta, and M. Hospital, *ibid.*, **32**, 943 (1976). [o] C. Cohen-Addad, *ibid.*, **29**, 157 (1973).

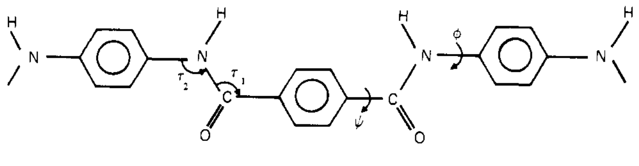
Table II
Bond and Torsion Angles in Crystalline Aromatic Esters

compd	τ_1, deg	τ_2, deg	ϕ, deg	ψ, deg	ref
phenyl benzoate	110.9	118.3	65.1	9.8	a
diphenyl p-phenylenediacrylate		119.6	65.0		b
dimethyl terephthalate	112.3			4.7	c
ethylene glycol dibenzoate	113.1			2.5	d
ethyl p-azoxybenzoate	119.9			1.5	e
trimethylene glycol di-p-chlorobenzoate	112.5			1.4	f
2,4-hexadiynylene dibenzoate	112.4			4.9	g
ethylene glycol bis(p-chlorobenzoate)	112.5			7.5	h
2-(4′-carbomethoxy-2′-nitrothiophenyl)-1,3,5-trimethylbenzene	112.0			6.5	i
2-(4′-carbomethoxy-2′-nitrophenoxy)-1,3,5-trimethylbenzene	118.8			11.9	j

[a] See ref 10. [b] H. Nakanishi and K. Ueno, *Acta Crystallogr., Sect. B*, **34**, 2036 (1978). [c] F. Brisse and S. Perez, *ibid.*, **32**, 2110 (1976). [d] S. Perez and F. Brisse, *ibid.*, **32**, 470 (1976). [e] W. R. Krigbaum and P. G. Barber, *ibid.*, **27**, 1884 (1971). [f] S. Perez and F. Brisse, *ibid.*, **32**, 1518 (1976). [g] A. W. Hanson, *ibid.*, **31**, 831 (1975). [h] S. Perez and F. Brisse, *Can. J. Chem.*, **53**, 3551 (1975). [i] S. P. N. van der Heijden, N. D. Chandler, and B. E. Robertson, *ibid.*, **53**, 2102 (1975). [j] J. P. N. van der Heijden, E. A. H. Griffith, W. D. Chandler, and B. E. Robertson, *ibid.*, **53**, 2084 (1975).



Type I



Type II

Figure 1. Planar forms of p-phenylene polyamides of types I and II. With NH replaced by O, the diagrams represent the corresponding polyesters. Torsional rotations about the NH–C_6H_4 and C_6H_4–CO bonds are denoted by ϕ and ψ, respectively. Skeletal bond angles τ_1 and τ_2 at CO and at NH, respectively, are indicated.

the monoanilides for which crystallographic data are available. In the calculations presented in the following paper,[7] we have used the rounded values τ_1 = 115° and τ_2 = 125° for the p-phenylene polyamides. In making these choices, little weight has been given to the data for the first entry in Table I in view of the exceptionally large value of ϕ. This large torsion suggests that intermolecular forces incident in this crystalline form affect the value of ϕ and, hence, may conceivably perturb τ_1, and τ_2 as well. The values chosen for these angles appear to be reliable within ±1°.

Only phenyl benzoate among the ester analogues for which structural data are compiled in Table II is a prototype of the p-phenylene polyesters. Values of τ_1 and τ_2 for this compound, given in the first row of Table II, were used in the calculations presented in the following paper.[7] They do not differ significantly from those for the other esters listed.

As expected, the torsional angles ϕ and ψ for the various examples of crystalline aromatic amides and esters in Tables I and II exhibit much greater ranges than the bond angles. These variations may be due, in part, to minor differences between the various compounds. Such effects should be small in as much as substituents have little effect on the torsion considered in each instance. Intermolecular forces peculiar to the packing in the crystalline forms of the various amides and esters probably are a source of

Table III
Parameters for Estimation of Nonbonded Interactions

atom[a]	ε, kcal mol^{-1}	$d^*/2$, Å	ref
H	0.06	1.50	19
C	0.116	1.50	19
C^{Ph}	0.06	1.95	19
C*	0.033	1.85	17
N	0.07	1.54	b
O	0.07	1.54	b
O*	0.07	1.54	17

[a] Carbonyl carbon and oxygen are identified by an asterisk. [b] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminiski, *J. Am. Chem. Soc.*, 91, 337 (1969).

greater variation in the values found for ϕ and ψ. Whereas the molecular form occurring in the crystal may generally be expected to approximate the conformation in which the intramolecular energy is minimized, significant departures from that form may occur in diverse crystals. These vitiating effects notwithstanding, the values of ϕ and ψ are generally concordant. For the amides $\bar{\phi}$ = 25° (±15°) and $\bar{\psi}$ = 26° (±3°). For the esters $\bar{\phi}$ = 65° and $\bar{\psi}$ = 6° (±4°).

Conformational Energy Calculations

These calculations were performed under the customary assumption that the molecular energy E can be evaluated as a sum of terms as follows:

$$E = E_{\text{nonbonded}} + E_{\text{strain}} + E_{\text{delocalization}} + E_{\text{Coulombic}} \quad (1)$$

The first term on the right-hand side comprises steric repulsions and London dispersion attractions between nonbonded atoms; the second term takes account of strain energies resulting from distortion of bond lengths and bond angles; the third term represents the energy of electron delocalization between the phenylene ring and the amide or ester group; and the last term is the repository for Coulombic contributions arising from the polarities of the functional groups. An additional "inherent" torsional energy is not required inasmuch as the torsional barrier for rotation about a C^{Ph}–R bond is known[14] to be negligible for a group R, such as methyl, that does not contribute significantly to electron delocalization and does not engage in steric interactions, i.e., in the absence of appreciable torsion-dependent contributions from the first and third terms in eq 1.

The first term in eq 1 was estimated in the customary approximation that the interaction between each pair of nonbonded atoms i and j depends only on the distance d_{ij} separating them. The contribution to the energy was calculated with the use of a two-parameter version of the "6-exp" empirical function published by Hill[15] and widely used for the calculations of conformational energies.[16-19] This function is

$$E_{\text{nonbonded};i,j} = \epsilon_{ij}[8.3 \times 10^5 \exp(-13.6d/d_{ij}^*) - 2.25(d/d_{ij}^*)^{-6}] \quad (2)$$

where d is the distance between the interacting atoms i and j and ϵ_{ij} and d_{ij}^* are parameters for the pair of atoms. The energy parameter ϵ_{ij} is taken to be the geometric mean of parameters ϵ_i and ϵ_j for the respective atoms. The characteristic distance d_{ij}^* is the arithmetic mean of "diameters" d_i^* and d_j^* assigned to the atoms. Values of these atom parameters used in the following calculations are given in Table III.

The Hill equation was adduced[15] for the express purpose of establishing correspondence between the "6-12" potential and the "6-exp" function in the range of low energies. Its origin as a hybrid of two empirical functions, one equipped with two parameters and the other with three, does not recommend it as a universal function of special merit for the calculation of nonbonded interactions, its subsequent widespread usage for this purpose notwithstanding. This function links the repulsive and attractive energies, making the one proportional to the other. Its inflexibility in this respect is unrealistic.

Table IV
Strain-Free Bond Lengths and Stretching Force Constants

bond	l_0, Å	$k_l \times 10^{18}$ J Å^{-2}
C=O	1.20	10.8
C–C*	1.50	4.4
C*–C^{Ph}	1.49	4.4
O–C^{Ph}	1.42	4.4
O–C*	1.33	5.1
O–C	1.44	5.4
N–C*	1.34	8.0
N–C	1.43	5.4
N–H	1.0	8.3

We chose to use eq 2 because of the availability of a computer program[19] allowing complete relaxation of bond angles, and of bond lengths as well, based on this function. The fact, established by numerical calculations, that it yields conformational energies for the n-alkanes in agreement with previous results,[20] and hence consistent with experiments,[21] lent assurance that computations carried out with the use of eq 2 should be satisfactory for our purposes. This appears to be another instance demonstrating that the particular functional form chosen to express nonbonded interactions is less important than its calibration.

The second term in eq 1 was represented by

$$E_{\text{strain}} = \tfrac{1}{2}\textstyle\sum k_l(l - l_0)^2 + \tfrac{1}{2}\sum k_\tau(\tau - \tau_0)^2 \quad (3)$$

with all bonds and all bond angles included in the respective sums. The strain-free bond lengths l_0 and bond angles τ_0 were so chosen as to reproduce the observed ("equilibrium") values of l and τ when used in conjunction with the array of force constants k_l and k_τ and the other parameters entering into calculations of the molecular energy according to eq 1.

The k_l and l_0 values are given in Table IV. For interactions involving esters, the former are taken from the work of Allinger and Chang[22] on aliphatic esters. The parameters involving the phenyl ring were taken from Andose and Mislow.[19] The k_l values for the amide group are based on the force constants deduced by Uno, Machido, and Saito[23] from infrared data on acetamide. The infrared constants were converted to force field parameters through multiplication by the ratio of k_l for C*=O to the infrared stretching constant. Differences between the calculated bond lengths and the strain free values are less than 0.02 Å.

Values of τ_0 and k_τ used in the calculations are given in the second and third columns of Table V. Bond angles, listed by number in the first column, are identified for the amides in Figure 2. Corresponding angles for the esters are denoted by the same number with a prime appended. Parameters for the esters are from the work of Allinger and Chang[22] on aliphatic esters. The k_τ for the aromatic amides were obtained by scaling bond angle bending constants from the infrared spectrum of acetamide[23] in the same manner as for the stretching constants; the proportionality is the ratio of the force field constant k_τ for C–C*=O bending to the infrared constant. Bond angles τ calculated by using the first two terms in eq 1 are given in the fourth column of Table V. They may be compared with the

Table V
Strain-Free Bond Angles and Bending Force Constants

bond angle	τ_0, deg	$k_\tau \times 10^{18}$ J rad^{-2}	τ, deg calcd	τ, deg obsd
1	120	0.50	118.7	118.4-120.9
2	120	0.20	120.2	
3	120	0.35	123.5	117.5-124.0
4	116	0.70[a]	121.0	115.5-119.1
5	122	0.57	118.7	119.0-121.2
6	122	1.53	120.2	120.8-124.0
7	124	0.65	123.2	121.6-126.0
8	117	0.46	120.1	
9	117	0.46	116.7	
10	107.8	0.24	108.2	
11	111.2	0.20	110.6	
12	120	0.50	118.5	116.0-119.6
13	120	0.35	122.7	121.7-126.0
14	117	0.46	115.8	
15	124	0.65	128.1	126.2-129.8
16	116	0.80	117.2	114.0-117.7
17	124	0.57	120.4	118.3-126.0
1′	120	0.50	118.7	118.9-122.8
3′	120	0.35	121.1	120.5-123.1
4′	114	0.70	114.5	110.9-112.8
5′	122	0.57	121.9	123.2-126.0
6′	124	1.13	123.6	122.1-124.0
7′	110	0.65	116.0	117.6-118.3
12′	120	0.50	119.7	122.0-123.0
13′	120	0.35	122.8	120.2-120.9
15′	116	0.65	119.6	118.3-119.6
16′	112	0.70	112.1	108.8-110.9
17′	124	0.57	122.6	126.0-127.3

[a] The k_τ indicated by the infrared data for acetamide[23] is unreasonably small. The value chosen is the same as k_τ (4′) for the analogous ester interaction.

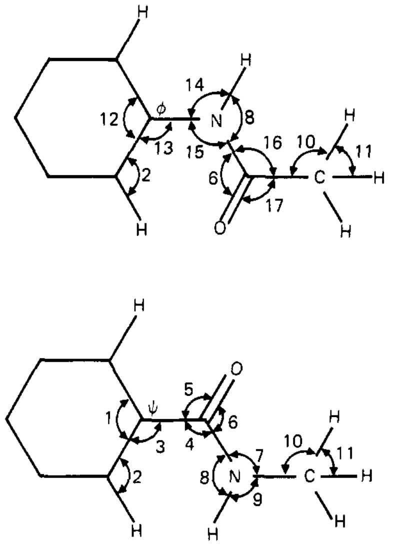


Figure 2. Bond angles in aromatic amides identified by number as denoted in Table V. The corresponding angles for esters are denoted in Table V by the same number with a prime appended.

ranges, given in the last column, of values found in X-ray crystallographic studies on the compounds identified in Tables I and II.

The electron delocalization energy was assumed to depend on the torsion angle according to

$$E_{\text{delocalization}} = -B_\phi \cos^2 \phi \qquad (4)$$

higher terms in the Fourier expansion being ignored. The corresponding expression was employed for the rotation ψ.

The Coulombic energy, represented by the last term in eq 1, may include permanent dipole–induced dipole interactions and, in compounds containing two (or more) amide groups, dipole–dipole interactions as well. The former contribute insignificantly to the torsion-dependent energy of the compounds considered and may therefore be ignored. The dipole moment of the amide group is 3.7 D, and it is directed approximately along the C═O bond.[21] The difference between the dipole–dipole interaction in the diamides of p-aminobenzoic acid in the anti ($\phi + \psi = \pi$) and cis ($\phi + \psi = 0$) forms is estimated to be on the order of 300 cal mol^{-1}, assuming an effective dielectric constant of 3. In the type II polyamide chains, the anti forms of the p-phenylenediamide and -terephthalamide residues are of lower energy than the cis forms, but the energy difference is approximately the same as that for type I. Thus, in both types the fully extended forms shown in Figure 1 are favored by dipole–dipole interactions. The estimated dipole–dipole interaction energy may conceivably be significant in the polyamides, according to calculations presented in the following paper.[7]

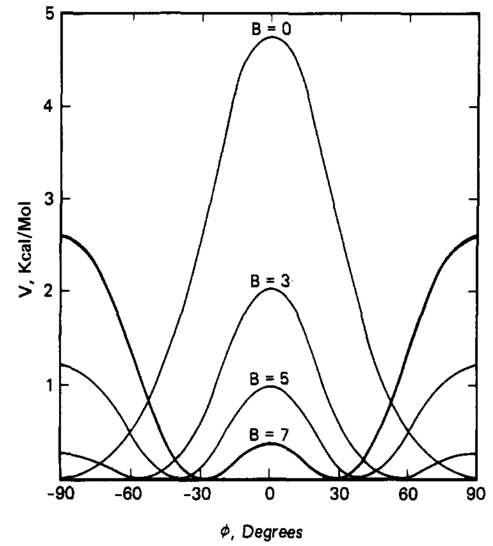


Figure 3. Conformational energies for acetanilide (AA) as a function of the torsional angle ϕ. Calculations (see text) were carried out according to eq 1–4; the delocalization energies B, in kcal mol^{-1} are indicated with each curve. Energies are relative to the minimum in each case. The curve for the preferred value of B is heavy lined.

The dipole moment of the ester group is about half that of the amide group and its direction is approximately perpendicular to the C^{Ph}–C* axis (the carbonyl carbon being denoted by C*). The magnitude of the energy difference between anti and cis forms is then on the order of 100 cal mol^{-1}, which is scarcely significant at the elevated temperatures required for experimentation on these polymers.

The Coulombic term in eq 1 has not been included in the calculations reported in the following section.

Results of Conformational Energy Calculations

Conformational energies of acetanilide (AA), phenyl acetate (PA), N-methylbenzamide (NMB), and methyl benzoate (MB) were calculated according to the first two terms in eq 1, using parameters specified above. With the torsion angle, ϕ or ψ, assigned a chosen value, all internal coordinates were allowed to relax to the configuration that minimized the energy, subject to the condition that the atoms of the amide or ester group remain copolanar and in the trans configuration. The pattern minimization procedure of Andose and Mislow[19] was employed for this purpose. The computations were repeated at intervals of 5° in ϕ or ψ. Results of these calculations are represented

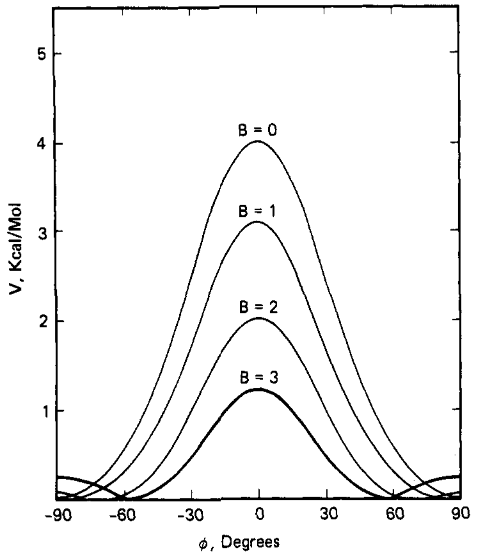


Figure 4. Conformational energies calculated for phenyl acetate (PA) calculated as a function of ϕ. See caption for Figure 3.

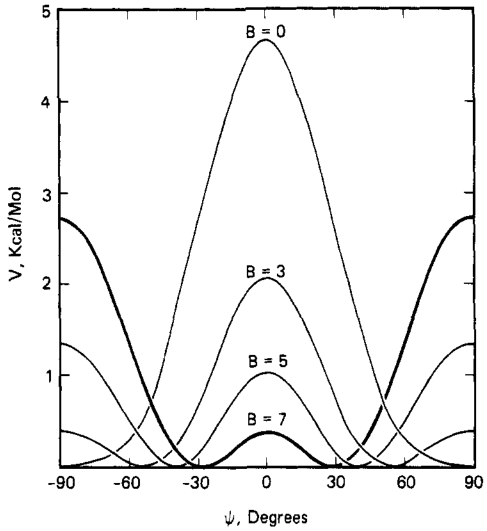


Figure 5. Conformational energies calculated for *N*-methylbenzamide (NMB) as a function of the torsion angle ψ. See caption for Figure 3.

by the curves labeled "$B = 0$" in Figures 3–6, respectively, for the four compounds above. The remaining curves were obtained for the values of B indicated in kcal mol^{-1} by adding $E_{\text{delocalization}}$ given by eq 4 to the $B = 0$ curve. The energy for each curve in Figures 3–6 is expressed relative to the conformation of lowest energy.

Steric repulsions between the carbonyl oxygen and the proximate *o*-hydrogen atom are large in the planar conformations ($\phi = 0°$) of AA and PA, as is evident from the curves for $B = 0$ in Figures 3 and 4. The dominant steric interaction in NMB involves the amide hydrogen and the nearer *o*-hydrogen. It produces a maximum of comparable magnitude at $\psi = 0°$; see the curve for $B = 0$ in Figure 5. The corresponding interaction is absent in MB. The much weaker repulsions between the carboxylate oxygens of this ester and the *o*-hydrogens are responsible for the small maximum at $\phi = 0$ in the $B = 0$ curve in Figure 6.

Approximate consistency with the X-ray results for anilides and benzamides is achieved by assigning the reasonable value $B = 7$ kcal mol^{-1} to the delocalization energy in the planar forms of the amides, AA and NMB. The curves thus calculated are heavy lined in Figures 3 and 5. They exhibit minima at $\phi \approx \pm 30°$ and $\psi \approx \pm 30°$, respectively, in satisfactory agreement with the crystallographic data in Table I. Heights of the maxima with torsion angle for the planar ($\phi = 0°$) and the perpendicular ($\phi = \pm 90°$) conformations of AA are estimated on this basis to be 0.4 and 2.6 kcal mol^{-1}, respectively. For NMB the corresponding barriers are calculated to be 0.4 and 2.7 kcal mol^{-1}, respectively.

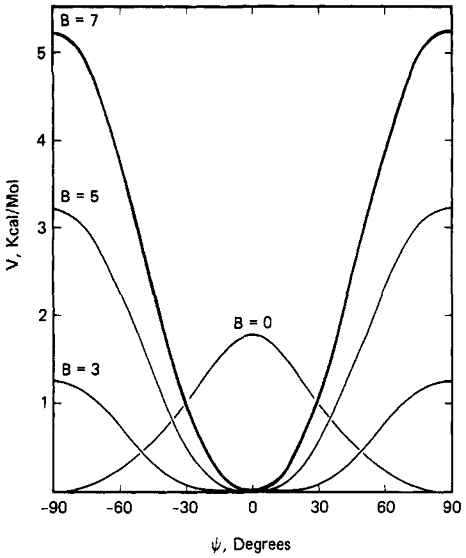


Figure 6. Conformational energies calculated for methyl benzoate (MB) as a function of ψ. See caption for Figure 3.

Agreement with the indications afforded by crystallographic results for PA (Table II) requires $B \approx 3$ kcal mol^{-1}. The respective barriers at $\phi = 0°$ and $\pm 90°$ for this value of B are 1.2 and 0.25 kcal mol^{-1}, as shown by the heavy-lined curve in Figure 4.

For MB, any value of $B > 3.0$ kcal mol^{-1} suppresses the low maximum at $\psi = 0°$ in the curve for $B = 0$; see Figure 6. Consistency with the small value of ψ indicated by crystallographic results in Table II is then established. The delocalization energy for benzoate esters should resemble that for the benzamides. On this basis, we take $B = 7$ kcal mol^{-1} for MB also. The rotational barrier for the perpendicular form ($\psi = \pm 90°$) thus calculated is 5.2 kcal mol^{-1}.

The molecular orbital calculations on aromatic amides carried out by Lauprêtre and Monnerie[12] by using PCILO methods yielded a minimum at $\phi = 0°$ and a maximum of ca. 8 kcal mol^{-1} at ±90°. Their results for the torsion ψ display a broad minimum over a range of at least ±30°, with a scarcely discernible maximum at $\psi = 0$. The height of the maxima at $\psi = \pm 90°$ is ca. 2 kcal mol^{-1}. Thus, the steric repulsions at $\phi = 0°$ and $\psi = 0°$, which structural data show unequivocally to be substantial, are not evident in these calculations. That these repulsion are indeed operative is demonstrated by the crystallographic results, summarized in Table I, indicating minima displaced some 30° from $\phi = 0$. Also, the height of the maxima at $\phi = \pm 90°$ according to the PCILO calculations seems much greater than could be attributed to the sacrifice of delocalization energy when the plane of the amide group is transverse to phenyl.

One of us (J.P.H.) has carried out ab initio molecular orbital calculations[13] on formanilide, phenyl formate, benzamide, and methyl benzoate with the use of the GAUSSIAN-70 program of Pople and co-workers[24] at the STO-3G minimal basis level. The lengths of the C^{Ph}–C^{*} and C^{Ph}–X bonds and the associated bond angles were optimized for selected values of ϕ and ψ. Details of the calculations will be published elsewhere. Here it may

Macromolecules 1980, 13, 484-491

suffice to point out that the results are in good agreement with the force field calculations presented in Figures 4 and 5 for aanalogous compounds and in Figure 6 for the same compound, methyl benzoate. Phenyl formate and benzamide exhibit minima displaced from the coplanar conformations ca. ±60° and ±30°, respectively; for methyl benzoate the minimum occurs at $\psi = 0°$, as in Figure 6. For formanilide, however, these calculations place the minimum at $\phi = 0°$, in agreement with the PCILO calculations of Lauprêtre and Monnerie[12] but at variance with the calculations presented in Figure 3. No explanation is apparent for this result of the ab initio calculations. It is incompatible with the X-ray crystallographic data on anilides (Table I), with the possible exception of those for para halogenated derivatives.

The GAUSSIAN-70 calculations yield a maximum of about 5 kcal mol^{-1} for the transverse conformation at $\phi = \pm 90°$. Although large, this barrier is more nearly in accord with expectation than the value indicated by the PCILO calculations.

References and Notes

(1) This work was presented at the ACS/CSJ Chemical Convention, Honolulu, Hawaii, April 2, 1979. A preliminary report appeared in *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**(1), 74 (1979).

(2) P. W. Morgan, *Macromolecules*, **10**, 1381 (1977); S. L. Kwolek, P. W. Morgan, J. R. Schaefgen, and L. W. Gulrich, *ibid.*, **10**, 1390 (1977); T. I. Bair, P. W. Morgan, and F. L. Killian, *ibid.*, **10**, 1396 (1977).

(3) S. P. Papkov, V. G. Kulichikhim, V. D. Kalmykova, and A. Ya. Malkin, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1753 (1974); S. P. Papkov, *Vysokomol. Soedin., Ser. A.*, **19**, 3 (1977).

(4) J. Economy, R. S. Storm, V. I. Matkovich, S. G. Cottis, and B. E. Nowak, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2207 (1976).

(5) V. V. Korshak and S. V. Vinogradova, *Usp. Khim.*, **30**, 421 (1961); V. V. Korshak et al., *Plast. Massy*, 9 (1962).

(6) V. N. Tsvetkov, *Vysokomol. Soedin., Ser. A*, **18**, 1621 (1976).

(7) B. Erman, P. J. Flory, and J. P. Hummel, *Macromolecules*, following paper in this issue.

(8) S. Harkema and R. J. Gaymans, *Acta Crystallogr., Sect. B*, **33**, 3609 (1977).

(9) W. W. Adams, A. V. Fratini, and D. R. Wiff, *Acta Crystallogr., Sect. B*, **34**, 954 (1978).

(10) S. Harkema, R. J. Gaymans, G. J. van Hummel, and D. Zylberlicht, *Acta Crystallogr., Sect. B*, **35**, 506 (1979).

(11) J. M. Adams and S. E. Morsi, *Acta Crystallogr., Sect. B*, **32**, 1345 (1976).

(12) F. Lauprêtre and L. Monnerie, *Eur. Polym. J.*, **14**, 415 (1978).

(13) J. P. Hummel, unpublished.

(14) H. D. Rudolph, A. Jaeschke, and P. Wendling, *Ber. Bunsenges. Phys. Chem.*, **70**, 1172 (1968). See also, *Z. Naturforsch., A*, **22**, 940 (1967).

(15) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(16) N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967); N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976).

(17) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

(18) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.* **19**, 531 (1968).

(19) J. D. Andose and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2168 (1974).

(20) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).

(21) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley-Interscience, New York, 1969.

(22) N. L. Allinger and S. H. M. Chang, *Tetrahedron*, **33**, 1561 (1977).

(23) T. Uno, K. Machida, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 897 (1969).

(24) W. J. Hehre, W. A. Latham, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSS/AN-70, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47401.

Moments of the End-to-End Vectors for *p*-Phenylene Polyamides and Polyesters

B. Erman[†] and P. J. Flory*

Department of Chemistry, Stanford University, Stanford, California 94305

J. P. Hummel

IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193.
Received December 21, 1979

ABSTRACT: Moments of rank 1–4 formed from the components x, y, and z of the chain vector $\mathbf{r}$ and expressed in the coordinate system affixed to the first unit have been calculated as functions of chain length n for *p*-phenylene polyamides of type I, $(\text{-NHC}_6\text{H}_4\text{CO-})_n$, of type II, $(\text{-NHC}_6\text{H}_4\text{NH-COC}_6\text{H}_4\text{CO-})_{n/2}$, and of the corresponding polyesters. Structural data on model compounds furnished the required geometric parameters. Configurational averaging was performed on the basis of the torsional potentials presented in the preceding paper. The persistence vector $\mathbf{a} \equiv \langle \mathbf{r} \rangle$ is dominated by its x component $\langle x \rangle$ along the phenylene axis; the transverse component $\langle y \rangle$ in the plane of this axis and the amide or ester group is negligible owing to the (approximate) mutual independence of torsions about a given phenylene axis; symmetry dictates that $\langle z \rangle \equiv 0$ perpendicular to this plane. The magnitude of the persistence vector depends sensitively on the difference δ between the skeletal bond angles at CO and at N or O. For the respective polyamides, with $\delta = 10°$, $\langle x_\infty \rangle = 410$ and 435 Å; for the polyesters, with $\delta = 7.4°$, $\langle x_\infty \rangle = 740$ and 785 Å. As n increases, the combined effects of departures of successive phenylene axes from parallelity and the random torsions introduce departures from the quasi-rod-like character manifested at comparatively small n. The chains become random coils at very large n (>2000 units for the polyamides). The course of the convergence of the distribution function $W(\mathbf{r})$ to its Gaussian limit, depicted by the higher moments, establishes the scaling factor m relating the number of units to the number of bonds in the corresponding freely jointed model chain. In the limit $1/n \rightarrow 0$, $m = 240$ units (1560 Å) for the *p*-phenylene polyamides and 450 units (2900 Å) for the polyesters compared with $m = 20$ (31 Å) for polyethylene.

Moments of the end-to-end vector $\mathbf{r}$ of the *p*-phenylene polyamides and polyesters discussed in the preceding paper[1] are the subject of the investigation reported here. These moments are significant as indexes of the character of the distribution $W(\mathbf{r})$ of vector $\mathbf{r}$. This distribution is determined, in principle, by the moments. Slow convergence of the expansion of $W(\mathbf{r})$ in its moments usually

---

[†] School of Engineering, Boğazici University, Bebek, Istanbul, Turkey.

0024-9297/80/2213-0484$01.00/0