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QUASI-STATIC MODELING OF CHAIN-DYNAMICS IN THE AMORPHOUS GLASSY POLYCARBONATE OF 4,4'-ISOPROPYLIDENEDIPHENOL

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Abstract: A detailed static atomistic model of the dense, glassy polycarbonate of 4,4'-isopropylidenediphenol ('bisphenol-A polycarbonate', PC) is used for a quasi-static simulation of localized motions. These motions include the phenylene ring 'flip', conformational changes of the carbonate group, and cooperative main chain motion. The frequency distributions for both simulated motions cover several orders of magnitude. The average energy barrier to phenylene ring 'flip' is calculated as 10.4 (± 6.7) kcal/mol and the average barrier for the conformational change of the carbonate group is 10.1 (± 6.5) kcal/mol. No significant reorientation of the ring axis was observed in the simulations, with 90% of the axes changing less than 15°. A slight main chain motion was found superimposed upon the ring 'flip' and the

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I. INTRODUCTION

The localized motions which occur in the glassy polycarbonate of 4,4'-isopropylidenediphenol ('bisphenol-A polycarbonate', PC) have been the subject of many detailed macroscopic and microscopic investigations using both experimental dynamic techniques and computational models. These studies frequently were focussed on the proposed link between the mechanical behavior of PC and chain motions occurring on the atomistic scale. Localized chain motions of interest include phenylene ring 'flips', conformational changes involving the carbonate group, and motions of the monomeric unit as a whole. The previous computational models employed to investigate these processes have been limited because of the absence of an accurate and detailed structural model of the polymer in the amorphous bulk state. Such a model now exists; static microstructures of PC[1] based upon a recently developed force field[2] have been generated by an energy *minimization* technique.[3] The analysis of these microstructures and comparison to experimental data suggested the suitability of using them for researching other phenomena occurring in PC.[1,4] Here we report on a study of the localized motions using the generated microstructures. These motions include the phenylene ring 'flip', conformational changes involving the carbonate group, and motions of the monomeric unit as a whole. Special emphasis was placed on investigating the influence of intermolecular packing in detail.

A quasi-static approach was employed; this is an approximation for simulating chain dynamics. In the dense, glassy state of amorphous PC it presents in our opinion currently the most reliable simulation technique to probe specific motions, considering that the characteristic time for a phenylene ring 'flip' is roughly 4 x 10^{-7} seconds at room temperature.[5] (A simulation on the order of several microseconds would be required using a deterministic molecular dynamics technique under these conditions to study the ring flip in the bulk; this is beyond today's computer resources.)

II. PREVIOUS WORK

The small scale motions that occur in PC in both the dilute solution and the solid states have been the subject of several studies. Theoretically and experimentally particularly well investigated are the conformational changes of single chains occurring in dilute solution and the effects of the purely intramolecular contributions to the motions that occur in PC.[6-17] Tonelli,[6] using molecular mechanics methods to study the conformational characteristics of the PC repeat unit, noted that this polymer had very low intramolecular rotational barriers and postulated that they could be related to its impact strength properties. Sundararajan,[7] and Tekely and Turska[8] studied the conformations of the PC repeat unit also with molecular mechanics tools and suggested that for a 180° 'flip' of a phenylene ring to occur, cooperative motion of the adjoining ring would be necessary in order to follow a low energy rotation path. Bendler,[9] Bicerano and Clark,[10,11] and Laskowski et al.,[12] utilizing various quantum mechanical techniques and again considering isolated chain segments, showed that their calculated energies were in accord with many experimental values assigned to localized motions postulated to occur in the bulk. (It must be noted here that studies considering solely isolated chain models account only for intramolecular energy contributions and are therefore of limited use in the application to bulk motions; they can aid in the understanding of what motions are implausible, but not necessarily in what motions are likely.)

The dilute solution behavior of PC and other structurally related polycarbonates has been experimentally studied by O'Gara et al.[13] and by

Connolly et al.[14] utilizing ^{13}C, proton, and ^{19}F NMR. Three different dynamic processes were distinguished; segmental motion, methyl rotation, and phenylene ring motion, and it was noted that for the polycarbonates with good impact strength, facile phenylene ring rotation occurred. Connolly et al. through experiments involving varying the concentration of the dissolved polymer, found that the segmental motion and the ring rotation were possibly cooperative; two different correlation functions for the segmental motion were considered, one based on the Weber-Helfand model,[15] and the other on the Jones-Stockmayer (crankshaft) model[16] of local jumps. Both approaches yielded fits of similar quality providing little additional information on the local dynamic processes.

Connolly, Gordon, and Jones[14] first introduced the idea of *cis,trans* isomerisation of the carbonate group as a mechanism for the ring rotation. This concept was expanded by Jones,[17] who described a mechanism through which ring rotation could occur: two neighboring carbonate groups (along the chain), one in a *cis,trans* (or *trans,cis*) conformation and the other in a *trans,trans* conformation can 'exchange' their conformational states. The orientation of the ring axis is approximately preserved in this process while the rings in between the 'exchanging' carbonate groups have undergone a 180° flip, the carbonate termini have also roughly retained their orientation. Similar concepts have been advanced by Tekely,[18] who combined a molecular mechanics conformational analysis of various fragments of PC chains with relaxation times of PC in solution to a conformational reorientation model where the carbonate group is held rigid. Sequential transitions between isomeric states of neighboring bonds of the chain were deemed likely to occur in solution and 'crankshaft' type motions should be less probable. Indeed, the isolated chain behavior has been investigated extensively and it is well characterized, but the information obtained has limited applications to the chain behavior in the dense, bulk state where intermolecular contributions can be large and possibly dominant (as we will demonstrate below). We will not further focus on solution properties of PC.

The solid state of PC has also been the subject of many inquiries, both experimental and theoretical and include both macroscopic and microscopic probes into the nature of dynamic processes.[19-50] PC is glassy, crystallizing only under special conditions, with a measured glass transition temperature of ca. 145 °C (differential scanning calorimetry or dilatometry).[19,20] In addition, ultrasonic absorption,[21] dielectric relaxation,[19,20,22,23] and dynamic mechanical spectroscopy,[20,22,23] tend to yield lower temperature transitions. Broad-line nuclear magnetic resonance (NMR) also has been used to measure low temperature transitions.[5,8,19,26-30]

Phillips et al.[21] record three temperature dependent processes by ultrasonic absorption measurements, the most prominent one occurring at 140°C (associated with T_g). There is a transition at roughly -100 °C and intermediate signals appear in partially oriented or crystalline samples at about +70 °C. The transition at -100°C has an activation energy of ca. 10 kcal/mol.

Dielectric relaxation measurements have been recorded by several researchers. Matsuoka and Ishida[19] found a secondary transition, located at ca. -120 °C, which was insensitive to crystallinity and temperature change and had an activation energy of 7 kcal/mol. Neki and Geil[20] found an additional peak at ca. 60 °C that disappeared with annealing, and resolved the band at about -100 °C into 2 peaks. Watts and Perry's results were similar;[22] they found that the 'low temperature peak' could be resolved into two asymmetric signals, with activation energies of 11 kcal/mol and 2-7 kcal/mol. Pochan et al.[23]

reported an additional peak at -53 °C which disappeared when plasticizer was added.

Dynamic relaxation spectroscopy experiments have been widespread. For comprehensive surveys of the mechanical and dielectric loss spectroscopy findings, the reader is referred to Yee and Smith[24] and McCrum et al.[25] In general the results include transitions at ca. 150 °C, a broad peak at ca. -100 °C that can usually be resolved into 3 bands, and an intermediate peak that is found at 80 °C. Boyer and Christiansen found that the peak at ca. -100 °C moves to room temperature with the application of 10 kbars hydrostatic pressure. More recently, Yee and coworkers[32,33] have used dynamic mechanical spectroscopy with copolymers of PC and related polycarbonates to study the scale of the localized motions and the proposed effects of hyperconjugation.

Microscopic probes into the behavior of PC that have been reported include infrared spectroscopy and extensive solid state NMR studies. Yannas and Lunn[34] have used infrared dichroism to study the chain backbone motion under stress and during isothermal annealing, and reported that chain back-bone motion occurs well below T_g.

Proton (^1H) NMR line shape and relaxation studies have produced valuable information on dynamic processes occurring in glassy PC, but these methods cannot describe the nature of the motions due to the complexity of the spectra. Using structurally related polycarbonates, however, can simplify the spectra considerably. Inglefield, Jones, et al.[35,36] studied chloral polycarbonate, which is similar in structure to PC except that it has no methyl hydrogens; the ^1H spectrum is simple enough to determine that a dominant motion in the observed frequency window is the phenylene ring rotation, where the 1,4-phenylene 'ring axis' does not undergo significant reorientation.

Spiess and coworkers[37-39] have used ^2H NMR spectroscopy to investigate deuterated PC, and concluded that the phenylene rings undergo 180° 'flips' in addition to low amplitude fluctuations of ± 15° (rms) about the same axis. They also indicate that the dynamic processes occurring in PC occur in a wide frequency band, and that significant reorientation of the main chain cannot be observed.

Similar results were obtained using ^{13}C NMR spectroscopy by Roy et al.;[40] analyzing the observed chemical shift anisotropy (CSA) these authors concluded that the rings underwent 180° 'flips' simultaneously with restricted rotation about the ring axis, and that the motions are governed by a broad distribution of activation energies.

J. Schaefer and coworkers[41-43] employing dipolar rotational spin echo ^{13}C NMR spectroscopy and ^{13}C CSA concluded that three characteristic motions take place in glassy PC below T_g: '180° ring flips' in which the ring axis does not undergo significant reorientation; '30° oscillations' of the ring about the same axis; and a '15° main chain reorientation' that occurs 'in concert' with the ring flip. They also noted that the ring flip occurs with a broad distribution of frequencies, but not amplitudes.

The changes in the carbonate group itself were studied by Henrichs et al.[44] using ^{13}C CSA; the resulting spectra were found to be independent of temperature and therefore not decisive, but the study did allow for limitations to be set on the type and scale of possible motions incorporating the carbonate group. Henrichs et al.[45,46] also investigated the ring 'flip' in low molecular weight crystalline analogs of PC using ^2H NMR spectroscopy. The results indicate that distortion of a carbonate group can facilitate the flipping motion of the neighboring phenylene ring and that the ring flip rate is strongly dependent on the local environment.

Recently, Walton et al.[47] conducted ^1H NMR line width experiments at various applied hydrostatic pressures, and concluded that ring 'flips' were suppressed by increased pressure. The average activation volumes calculated from the pressure dependence were about 10% of the repeat unit volumes, or about 1/3 the volume of a phenylene ring.

Two- dimensional ^2H NMR has been utilized by D. Schaefer, Spiess and coworkers to investigate ultraslow molecular motions present in glassy PC which have correlation times on the order of milliseconds to seconds.[48] The phenylene ring flips occurring below 0° C are not of exactly 180° but have a rather ill-defined distribution of reorientation angles centered about 0° and 120°. The distribution changes with applied mechanical stress.

Simulations of the structure of and the molecular motions in glassy PC have been carried out invoking models of varying complexity. The 'Strophon' model of Yannas and Luise[49] was one of the earliest approaches and consisted of a molecular level model which assumes hexagonal packing of quasi-lattice sites with spherical symmetry. Yannas and Luise used the Strophon model to study the mechanisms for local chain motion for various phenomena in PC and other polymers and concluded that the relationships between chain stiffness and intermolecular interactions determine the mechanisms by which the polymer chains move under an applied stress. At 0 K, the intermolecular forces in PC were found to dominate the chain dynamics.

J. Schaefer, Perchak, and coworkers[42,50] researched the ring 'flip' mechanism with a model consisting of a two dimensional lattice of interacting phenylene rings. The Brownian motion model lead to the conclusion that the ring 'flip' is determined by the flexibility of the lattice; this is in substantial agreement with the later experimental findings of Henrichs et al.[46] Fischer et al.[51] modeled PC as 'bundles' of parallel segments, two repeat units long. Such a bundle-model yielded computed neutron scattering results in close agreement with experiment. In the latter two studies where the ring motions were studied in the bulk state the structure of glassy PC was thought to have considerable short range order, similar to a liquid crystalline state. In a companion study[1] referred to below as (II), however, a model with atomistic detail of the bulk was obtained for dense PC. One important result of that simulation model was that the structure is highly amorphous on the length-scale of the simulation (18.5-30 Å) with only very limited intermolecular correlations.

III. MODELING OF CHAIN MOTIONS

Amorphous PC microstructures were generated by the modeling technique described in (II). These represent static models of dense, disordered packings of density appropriate to a temperature of 300 K, and of minimum (local) potential energy. The microstructures can be described as 0 K models at a density corresponding to the temperature of interest. Thermal motion is included in the structures only in an average fashion through the volume available to the atoms. We use these static structures here as model media to study molecular motions.

The method of investigation involves: starting with an energy minimized structure in which one degree of freedom is selected, changed by a small amount, held fixed at the new value while all other degrees of freedom in the system are systematically adjusted to again minimize the potential energy of the microstructure, subject, however, to the condition that the chosen degree of freedom remains unchanged. This new state is generally of higher energy than the starting structure and is said to represent a 'constrained minimum'. It is, of course, equally possible to slightly change several degrees of freedom simultaneously in a concerted way and to subsequently minimize the potential energy of the system keeping all (or some) of the altered degrees of freedom fixed. By repeating this process of small imposed microstructural changes and constrained minimization, a path in the overall potential energy is traced out in configurational space. This path will, by necessity, follow at first a trajectory of continuously increasing energy, but will ultimately lead to a saddle-point at which the potential energy reaches a maximum with respect to the 'driven' degree(s) of freedom and at a minimum with respect to all others. Further change in the constrained degree(s) of freedom will lead to lower energies. It is tempting to associate the path traced in configurational space by this procedure with the system trajectory during a conformational change in the dense system. Clearly, this would imply that a very slow process (slow on the time scale of vibrational molecular motion) were to be approximated. Indeed, the experimental mean frequencies of the motions modelled here (e.g., the phenylene ring 'flip') are known to be low, and at room temperature are in the range of MHz. In comparison we recall that the frequencies of vibrational molecular motions are 3 to 6 orders of magnitude higher. We therefore tentatively identify the increase in potential energy from the unconstrained 'ground state' to the saddle-point with an energy barrier ($E^‡$) over which the system has to be activated, and estimate the mean frequency of transition by

$$\nu = \nu_0 \frac{Q_{SP}}{Q_{GS}} \exp\left(-E^‡/RT\right) \tag{1}$$

where ν_0 is the characteristic frequency of the phenylene ring oscillating in its energy well as a rotational simple harmonic oscillator, and where the activation entropy is approximated by the ratio of the relative partition functions (Q_{SP}/Q_{GS}). The ratio of the partition function is assumed to be unity. We obtain an estimate of the frequency ν_0 directly from the curvature of the local energy well of the ring.

As an illustration, we consider the 'flipping' of a phenylene group: Figure 1 shows the PC repeat unit. The torsion angles of interest are φ_2, which is the torsion angle between the isopropylidene group and the phenylene ring, and φ_3, which is the torsion angle between the phenylene ring and the carbonate group. These two angles will be denoted as types A and B, respectively. The schematic in Figure 2 clarifies the simulation technique. Starting from a fully minimized microstructure, a single phenylene ring is selected and rotated by changing its associated torsion angle an incremental amount in such a way, that the entire structure remains the same except for the position of the phenylene ring. The torsion angle preceding the phenylene ring is then 'fixed', and the remainder of the system is subjected to an energy minimization.

During this procedure, when one (or several) torsion angle(s) is (are) driven, the other torsion angles of the system undergo some adjustments in order to minimize the energy in conformity with the applied constraint. When a type A torsion angle is driven, it is the adjoining phenylene ring that rotates most, whereas when a type B torsion angle is driven, either the adjacent phenylene ring undergoes a significant rotation, or (most often) the adjoining carbonate group undergoes a sizable conformational change, or a combination of the two occur.

Two of the 13 generated microstructures were chosen at random for the detailed simulations. All bonds of type A and B from one structure were driven until the saddle point conformations were found for each case as well as several from the second structure so that a total of 60 energy barrier 'events' were probed. Incremental rotation steps up to 20° were selected. For a step of 20°, the minimization routine requires approximately 300 iterations to reach a new 'constrained' minimum; fewer iterations were necessary for smaller steps.

It is important to distinguish between molecular changes in internal coordinates and those with respect to an external frame of reference. As internal coordinates relevant for the aspects investigated here we have employed the torsion angles of the chain, as defined in Figure 1. The torsion angle φ, associated with a given change has always been referred to the conformational reference state given in that figure. The external coordinate frame is the one defined by the edge vectors of the 'box' that specifies the spatial continuation conditions. The *reorientation angle* $\Delta\alpha$ is the angle between the normal vectors to the phenylene ring (Figure 3) or between vectors along the C=O bond in the carbonate moiety (Figure 4) before and after a procedural step of 'driving' the rotating entity (see above). Computed in its external coordinate frame, its integral, α, of the reorientation angle was always calculated from the 'ground state', i. e., the structure of the unconstrained minimum system. We denote a simulated motion as a 'ring flip' if α changes significantly for the ring investigated and is much larger than the change of α for the carbonate moiety.

IV. RESULTS

4.1 Phenylene Ring 'Flips'

A typical sequence of events is displayed in Figure 5 for the case where the torsion angle between an isopropylidene group and an adjoining phenylene group (type A angle) is 'driven'. It shows the increase of the system potential energy with reorientation angle (α) for the third ring along the chain. In this case, the torsion angle has been 'driven' a complete 180°.

During the initial steps of the simulation before the energy of the system peaks, the conformational changes that occur in the entire structure are fully reversible upon inversion of the change in the 'driven' degrees of freedom, indicating that the system has undergone a series of 'quasi-static' displacements that lead to a new equilibrium state. Up until the first maximum in energy, if the structure is minimized without constraints, it reverts to the initial minimum (the 'ground state'). However, after the first maximum in energy, the conformational changes are not reversible and if the system is minimized without constraints, a 'new' minimum energy structure is found. The non-equilibrium decay that occurs after the energy maximum is by necessity not a realistic rendition by the computer of physical events. In the computer simulation experiments energy minimization is the only possible means of making connection between adjoining stable structures or states. Therefore, during the simulation we are concerned only with the conformational changes that occur up to the first maximum in energy, over the concave portion of the potential energy contour. It is expected that the maximum that has been reached constitutes an effective inflection point and that any convex portion of the energy contour might not be accessible to the simulation. Therefore, we consider the peak energy barriers obtained by our simulations as lower bounds to the actual saddle point energy.

The influence of the step size, $\Delta\varphi$, on the results was investigated. The same equilibrium conformation for a given φ was found along the simulation path regardless of the size of the angular increments used to get there ($\Delta\varphi \leq 20°$) indicating that the minimum energy structures found (before the system energy peaks) are independent of the step size, and constitute a relatively unique description of the potential energy contour.

In the 30 simulations where type A angles were 'driven', the predominant process was an adjoining phenylene ring 'flip'. The 30 simulations where a type B angle was 'driven' resulted in 8 'flips' of the adjoining phenylene rings, and in the remainder of the cases, resulted in conformational rearrangements involving the adjoining carbonate group, which is discussed below. In most cases (30 out of 38), the shape of the curve E_{pot} versus α was fitted well by a parabolic expression of the type

$$E_{pot} = a\alpha^2 \qquad (2)$$

The 'steepness' parameter a, (or the local curvature of E_{pot} with the generalized coordinate α) is important for a discussion of the oscillatory motions of the phenylene ring, and is necessary for an estimate of the characteristic frequency ν_0 in Eqn. (1). The average value of a was found to lie in the range of $6.94 \leq a \leq 52.5$ kcal/mol rad^2 with a mean of a = 23.0 (± 10.1) kcal/mol rad^2, where the value in parenthesis is the standard deviation. Figure 6 shows the cumulative distribution and the frequency distribution of the curvature parameters a obtained from the simulations of the phenylene ring 'flips'.

The mean value of the energy barrier for 38 ring 'flips' (30 from the fixing of type A angles and 8 from type B angles) is (standard deviation in parenthesis) Δ E = 10.4 (± 6.7) kcal/mol. The cumulative distribution of the peak energy barriers that was computed and found to fit rather well to a Weibull function is shown in Figure 7 together with its derivative giving the frequency distribution of barrier energies. The energy distribution can be transformed into a distribution of frequencies via Equation 1 using $\nu_0 = 2.3 \times 10^{12}$ Hz (for calculation see below). The resulting plot, depicted in

Figure 8. indicates an exceedingly broad distribution of frequencies, covering many orders of magnitude.

4.2 Conformational Changes in the Carbonate Group

When the torsion angle between a carbonate group and a phenylene group (type B angle) is used as the independent variable in the simulation, the system responds differently depending on what conformational change is energetically more favorable: the adjacent ring can rotate creating a ring 'flip', or the carbonate group can significantly change its conformational orientation, or a combination of the two can occur. The intermolecular packing about the torsion angle is the deciding influence on whether the ring will 'flip' or the carbonate group will change its conformation. The carbonate group changes its conformation through changes in the inner torsion angles (angles φ_4 and φ_5 in Figure 1). In 8 of the 30 simulations where type B torsion angles were 'driven', ring rotation was the primary conformational change. These cases were included in the ring 'flip' analysis presented above. In the remaining 22 simulations, in 15 cases the carbonate group primarily underwent a conformation change while in 7 a combination of both occurred.

Figure 9 shows the change in system energy due to a change in the second carbonate group along the chain resulting from 'driving' the succeeding C^{ar}-O bond where the independent variable is the reorientation angle α, shown in Figure 4. Similar to the cases of ring flip, the system goes through states of stable equilibrium up until the first energy maximum is reached. Here also the conformational changes were independent of step size in the region of stable behavior. For this particular simulation the torsion angle has again been rotated 180° for purposes of illustration only. As with the ring flip case we are interested only in the reversible changes of the system that occur before the first energy maximum is reached. In this range for the majority of the carbonate group conformational changes (8 out of 15) the form of the dependence of the potential energy E_{pot} on the angle α also fits a parabolic type function, with the curvature coefficient a of Eqn. (2) being in the range of $7.78 \leq a \leq 28.5$ kcal/mol rad^2 with a mean of $a = 12.7$ ($\pm$ 6.87) kcal/mol rad^2. The cumulative distribution and the frequency distribution of the energy curvature coefficient a for the carbonate group rearrangements is given in Figure 10, fitted to the best empirical Weibull distribution.

The mean value for the energy barrier for carbonate group rearrangements obtained from 15 simulations is $\Delta E = 10.1$ ($\pm$ 6.5) kcal/mol. Figure 11 shows the distribution of barrier energies for the carbonate group conformation changes, which is also fitted to a Weibull distribution for purely empirical reasons, followed by differentiation to obtain the frequency distribution.

V. DISCUSSION

5.1 Effects of Intermolecular Packing

The strong influence of the chain packing is evident in the energetics of the analyzed motions. The intramolecular energy barrier for a ring flip, calculated employing the force field used for this simulation on diphenylcarbonate and 2,2-diphenylpropane, is on the order of 3 kcal/mol,[2] indicating that intermolecular interactions are largely responsible for the energy barrier of the order of 10.4 kcal/mol in the dense, glassy state. The intramolecular energy barrier for conformational change in the carbonate group, based on diphenylcarbonate calculations, is 4 kcal/mol.[2] Again, this is much lower than the average value of 10.1 kcal/mol obtained in our simulations for the bulk material. In addition, the wide distribution of the energy barriers or alternatively the relaxation frequencies evident in Figures

7, 8, and ~~11 have~~ their origins in the variety of local environments governed by intermolecular interactions and the strength of molecular packing influences.

The effects of simply rotating one ring in the structure are far reaching. A direct visualization of this effect is given in Figure 12 where the molecular microstructure of the simulation cell is displayed at two different points along a 'rotation path' (hydrogens have been omitted and the atomic radii have been shrunk to permit a view into the entire cell); In Figure 12 the faint pattern (without the cross hatching) shows the initial configuration of the system ($\alpha = 0^\circ$), while the bold pattern gives the configuration at the peak energy ($\alpha \approx 55^\circ$). The 'driven' ring is shaded black, and the torsion angle that was 'driven' lies to the left of the shaded ring and is identified with an arrow. As expected, there is widespread rearrangement of the torsion angles all along the chain and, in fact, over the entire simulation cell. There is also significant cooperativity in motion of the driven ring with the phenylene ring across the isopropylidene group as is readily apparent. In addition, and unexpectedly, there are considerable adjustments occurring farther away from the 'driven' ring in apparently 'soft' regions. As an example, a carbonate group (circled in the Figure) relatively far away from the 'driven' ring undergoes a large conformational rearrangement apparently in sympathy with the driven ring. These changes are emphasized in Figure 13 where the difference between the values of the torsion angles of the chain between the initial conformation (faint pattern in Figure 12) and the conformation of the energy peak (bold pattern in Figure 12) are displayed. The 'driven' torsion angle is $\varphi 9$ (identified with the arrow). From the graph it is evident that the torsion angles close to the 'driven' angle change considerably, and that, while most of the other angles change by very small amounts, a chain segment located around $\varphi 40$ also exhibits large changes as well as a group around φ_{60}. These torsion angles around φ_{40} correspond to the carbonate group circled in Figure 12. This particular carbonate group is far from the intramolecular *trans,trans* energy minimum and resides in a very broad local potential energy well. Upon examination of other ring 'flip' simulations, it was found that this same carbonate group frequently changed conformations, regardless of how (spatially) far or close it was to the 'flipping' ring. It is evident therefore that this carbonate group represents a rotationally 'soft' region in the structure, and demonstrates that the effects of a ring 'flip' are generally very far reaching in the structure, much more so than previously appreciated and can often stimulate systematic responses far away from the main conformational change when such regions can be readily stimulated.

The data shown in Figure 13 also point to the effect of the cube size on the simulation: every torsion angle of the chain changes at least a few degrees during the 'flipping' of one ring. This indicates that the size of the domain affected by a ring 'flip' is larger than the size of the simulation cube itself and to some extent limits quantification of the long range effects of the ring flip. It is safe to conclude that the effects of the ring flip are far reaching going beyond a distance of ca. 10 Å.

While the intermolecular interactions dominate the energetics, the influence of the intramolecular interactions on the investigated dynamic process are strong as we already concluded in (II). As an illustrative example of the path determining influence of intramolecular interactions we consider in detail two angles in an isopropylidene moiety. The torsion angles of interest are φ_1 and φ_2 of Figure 1. These two angles can only move in a very cooperative manner due to intramolecular constraints.[2] Figure 14 contains a potential energy contour map for 2,2-diphenylpropane as the background field for the above two torsion angles as they advance the system along the reaction paths, and shows the local intramolecular energy contribution to the total energy along the two paths in configurational space. The intramolecular minima and energy barrier pathway are, respectively, represented by the × symbols and by the dotted line. Also included in Figure 14 are the actual paths taken during several different ring 'flip' simulations, where the end of the path indicated by the empty symbol is the starting position of the system, and the position marked with a filled symbol is the last simulated point, after the energy peaks were reached. The figure shows that the starting positions of the torsion angles at the initial system energy minima are not near the intramolecular minima (already emphasized in II) and that the paths significantly differ from what the purely intramolecular contributions would suggest. However, the high energy intramolecular interactions clearly make large domains in the map inaccessible. The strong influence of the intermolecular interactions largely determine the height of the energy barrier and the conformational path that the system takes in conjunction with the strong repulsive intramolecular effects.

To illustrate the carbonate group conformational alterations we consider the second carbonate group along the chain (the potential energy of this group as a function of the adjoining C^{ar} - O angle is plotted in Figure 9) here as an example. Figure 15 depicts the molecular microstructure at two different points along the rotation path. The faint pattern in Figure 15 represents the state at the third point of the rotation path ($\alpha = 23^{\circ}$) of Figure 9 and the bold pattern represents the fifth position ($\alpha = 63^{\circ}$). The torsion angle that was driven is identified with an arrow. For this particular range of the simulation the system undergoes fewer conformational changes than for the previously described ring 'flip' simulation, indicating the large variations of behavior that are possible. No 'soft' spots could be seen in this simulation, which is a trend that other carbonate group conformational change simulations follow. In Figure 16, the energy pathways of several simulations where the carbonate group changes conformation are superimposed on a potential energy contour map of the intramolecular interactions that occur in diphenylcarbonate due to changes in angles φ_4 and φ_5 (the torsion angles represented in Figure 1). Similarities to the ring flip simulations are obvious. Again, the 'starting positions' are not near the intramolecular potential minima, and the pathways do not follow their intramolecular minimum energy-increase counterparts, since these are primarily governed by intermolecular contributions to the energy change.

5.2 Angular Oscillations

The potential energy of the simulated microstructures as a function of the displacement in the 'driven' angle was mostly found to fit quite well to a quadratic, both for the ring flip and the changes in the carbonate group. The root-mean-square average angular displacement of the ring 'flip' and of the carbonate group conformational change was calculated to be 6.5° and 8.7°, respectively at 300 K. The associated oscillatory frequency for the ring 'flip', by use of a classical simple harmonic oscillator model, was found to be 2.3×10^{12} Hz.[52] This was the frequency used in calculating the relaxation frequency distribution in Figure 8.

5.3 Intramolecular Cooperativity of Chain Motions

Two distinct elementary dynamic processes have been studied in detail: the phenylene ring 'flip', and the carbonate group conformational change. For the phenylene ring 'flip', strong cooperativity across the isopropylidene group between the two adjoining rings has been found which is largely of an intramolecular nature and is of widespread occurrence, as demonstrated in

Figure 14. Other types of cooperativity along the chain have also been observed; they vary greatly in type and strength due to the influence of the dense packing. The most prevalent case being when a ring and the neighboring carbonate group move simultaneously. When a carbonate group is forced to change conformation, the phenylene rings on both sides have on occasion been observed to rotate, indicating that cooperativity can occur over more than one repeat unit.

A cooperative process proposed by Jones,[13] involving the conformational exchange between carbonate groups across a bisphenol-A group, did not occur in any of our simulations, and based upon the present set of data and the density of the packing, it seems an unlikely mechanism because of the distance between these groups and the degree of intermolecular cooperativity that would be necessary.

5.4 Main Chain Motion

'Main chain motion' was chosen to be represented by movements of the bisphenol-A moiety as a whole. It was monitored by considering either the movement of the isopropylidene group that is bonded to the 'driven' phenylene ring for the case of the ring 'flip', or alternatively as the movement of the isopropylidene group of both the neighboring bisphenol-A units for the simulations where the carbonate group changes conformations. Since the bond angles and the bond lengths were kept fixed, the isopropylidene unit moves exactly like the rest of the bisphenol-A units. Therefore, the motion analyzed was the main chain movement that occurred simultaneously with the nearby ring 'flip' or the nearby carbonate group conformational change. In the cases where rings 'flipped' the process was predominantly 'rocking' in nature, where the bisphenol-A group rotated about an axis parallel to the chain backbone (i. e. parallel to the O-O axis), and the rms average of the main chain motion was ca. 13° (67% of all moieties change less than 15°). For the cases where carbonate groups changed conformations, the rms average magnitude of the motion of the neighboring isopropylidene groups were ca. 11° (80% of changes were less than 15°) with no specific motion predominating.

It should be noted that all of the above results indicate that the ring 'flip' changes the structure more than carbonate group motion. Although the energy barriers calculated for the two types of motions are very close, the angular displacement analysis for the carbonate group showed it to be 'softer', with the energy 'wells' being broader for the carbonate group conformational change than for the ring 'flip'. Visual inspection of Figures 11 and 16 also demonstrates this difference.

5.5 Comparison with Experiment

The simulation results compare very well with the experimental results. The energetics of our ring 'flip' calculations agree well with the reported experimental NMR activation energies of 9.1 and 12.0 kcal/mol.[40,47] The calculated values are also similar to the energy barrier associated with the low temperature (~ -100° C) dynamic mechanical loss peak which is approximately 10 kcal/mol.[21] This match, however, may be completely coincidental and does not necessitate the conclusion that the motions simulated are in any way correlated with the mechanical transitions. Such possible correlations are the subject of a separate simulation to be reported later. The activation energy calculated for the low temperature dielectric relaxation (~ -100° C) is about 7 kcal/mol.[16] Upon inspection of the frequency distribution shown in Figure 8, comparison of calculated activation energies with experimental activation energies must be approached with caution. The broad distribution of the energy barriers that occur in both types of simulations are in accord with the observations of several researchers who have found that NMR indicates that the distribution of the frequencies of motions are inhomogeneous and very broad.[35-40] When considering the frequency distribution of the ring 'flip' (Figure 8), it is apparent that the distribution is very broad at room temperature, covering several orders of magnitude in frequency. If the distribution is fitted to a stretched exponential function of the form[40,53]

$$P(t) = \exp\,(-t/\tau)^{\beta} \qquad (3)$$

the value for β is between 0.1 and 0.2 for both the ring 'flip' and the carbonate group conformational change, again indicating the extreme breadth of the distributions. The breadth of the simulated distribution is exceedingly large, and leads to the finding that it is not possible to get a conclusive measure of this breadth of activation energy by experimentally stimulating the structure since no experimental technique has a frequency window large enough to cover the necessary ca. 15 orders of magnitude.

An important feature that can be extracted from experiments is the change in direction of the ring axis when either the ring 'flips' or the carbonate group changes conformation. Experiments have shown that the ring axes do not significantly reorient in space.[33-40] In our simulation this is indeed the case; when the ring 'flips', the ring axis changes by less than 15° in 87% of the simulations. In the cases where the carbonate group changes conformation, the orientation of the phenylene rings on either side of the carbonate group of interest also change by less than 15° for 87% of the simulations. This is an important feature when considering the plausibility of the carbonate group motion. Since NMR has not conclusively measured the presence or absence of such a motion,[41] the possibility of carbonate group conformational changes as described here are not contradictory of the NMR experimental findings.

The intramolecular cooperativity of neighboring molecular segments in bulk PC has not been measured directly. However, for low molecular weight crystalline analogs of PC, it was suggested that the environment around the ring and the ability of the carbonate group to deform greatly influences the ring motion.[42-44] This experimental finding is mirrored in the majority of the ring 'flip' simulations: ring rotation frequently occurs with some type of deformation to the neighboring carbonate group. Recent dynamic mechanical studies also indicate that the dynamic processes in glassy PC involve more than one repeat unit.[30,31] This type of behavior is found in the simulations in that the rings across the carbonate group rotate as the carbonate group changes conformation, and in that both bisphenol-A units adjacent to the carbonate residue move as the carbonate group changes conformation.

Another type of intramolecular cooperativity that some experiments indicate occurs in glassy PC is main chain motion concurrent with the ring flip.[54] As mentioned above, when the carbonate group changes conformation, the neighboring bisphenol-A moieties on either side 'wiggle'. Specifically for ring 'flips', some main chain motion in the simulations is present, dominated by a slight rocking movement of the bisphenol-A residue as a whole. Our results are in good agreement with Poliks et al. who report that the rms amplitude of main chain rotation in PC is less than 20°.[43]

Since the simulations were preformed at constant volume and atomic level internal stresses were not monitored during the simulations we find comparison of activation volumes not possible with published experimental measurements.[47]

VI. CONCLUSIONS

The quasi-static simulation of chain dynamics in dense, glassy PC has proven to be useful in the modelling of chain dynamics. Specifically, the phenylene ring 'flip' and the carbonate group change of conformation have been simulated and the response of the structure studied in detail. The results are in good agreement with experiment and indicate a broad variety of features, most prominent among them are the extremely wide distribution of transition frequencies for ring 'flip' and conformational changes in the carbonate group. The extreme breadth of these distributions indicate that experimental activation energies must relate only a fraction of relaxation processes in the lower end of this wide spectrum of processes that the structure can kinematically undergo.

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(52) The energy change ΔE_{pot} with the rotation angle α defines a restoring moment M of the ring group of atoms in their energy well. The phenylene ring can be viewed as a simple harmonic oscillator performing rotational oscillations in its energy well when perturbed. The resulting characteristic rotational frequency ν is given by:

$$\nu_o = \frac{1}{2\pi}\sqrt{\frac{K_r}{J}}$$

where K_r is the rotational restoring spring constant and J is the effective mass moment of inertia of the ring. K_r can be given as:

$$K_r = \frac{dM}{d\alpha} = \frac{d^2\Delta E}{d\alpha^2} \cong 2a$$

where *a* is the curvature of the energy well for the ring oscillator presented in Figure 6.

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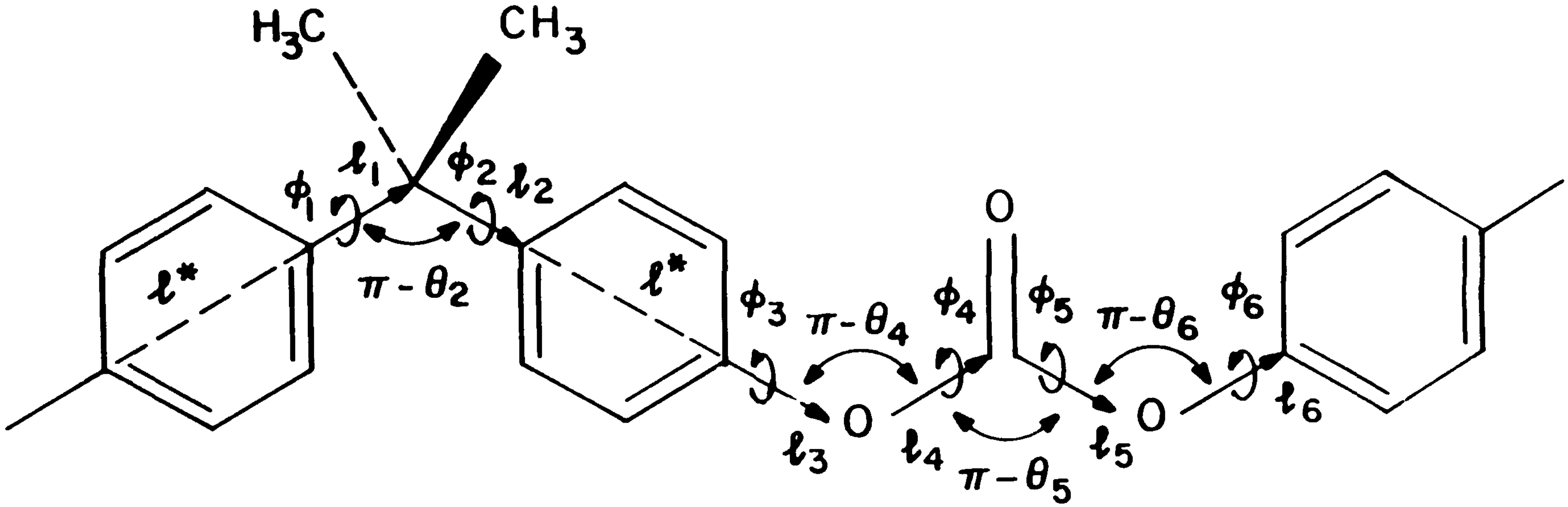
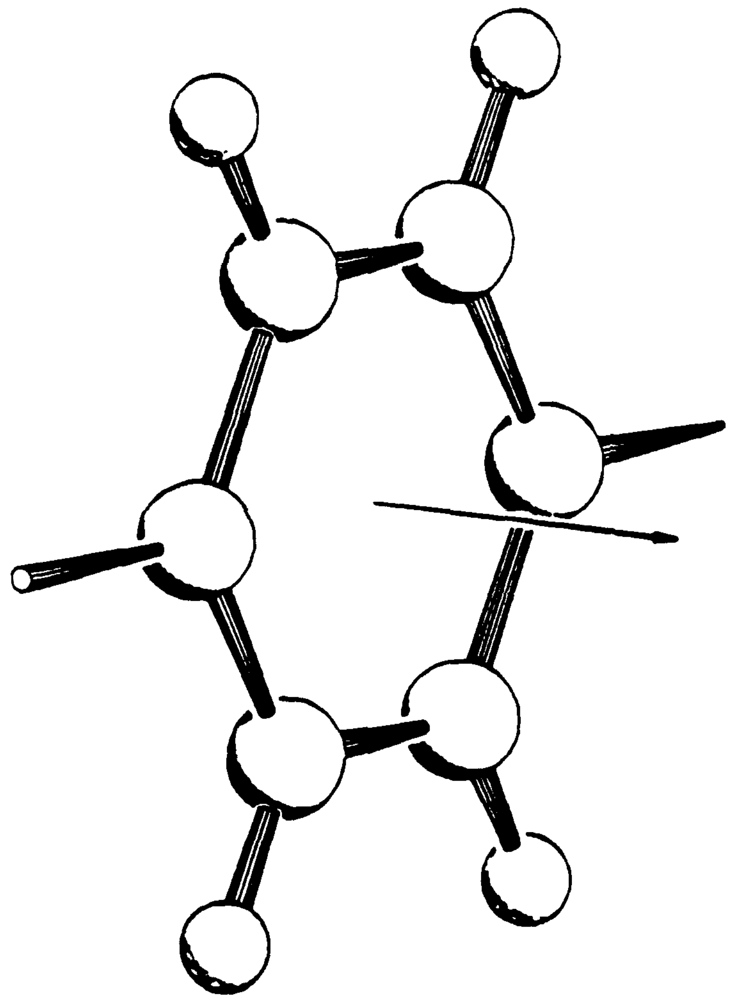
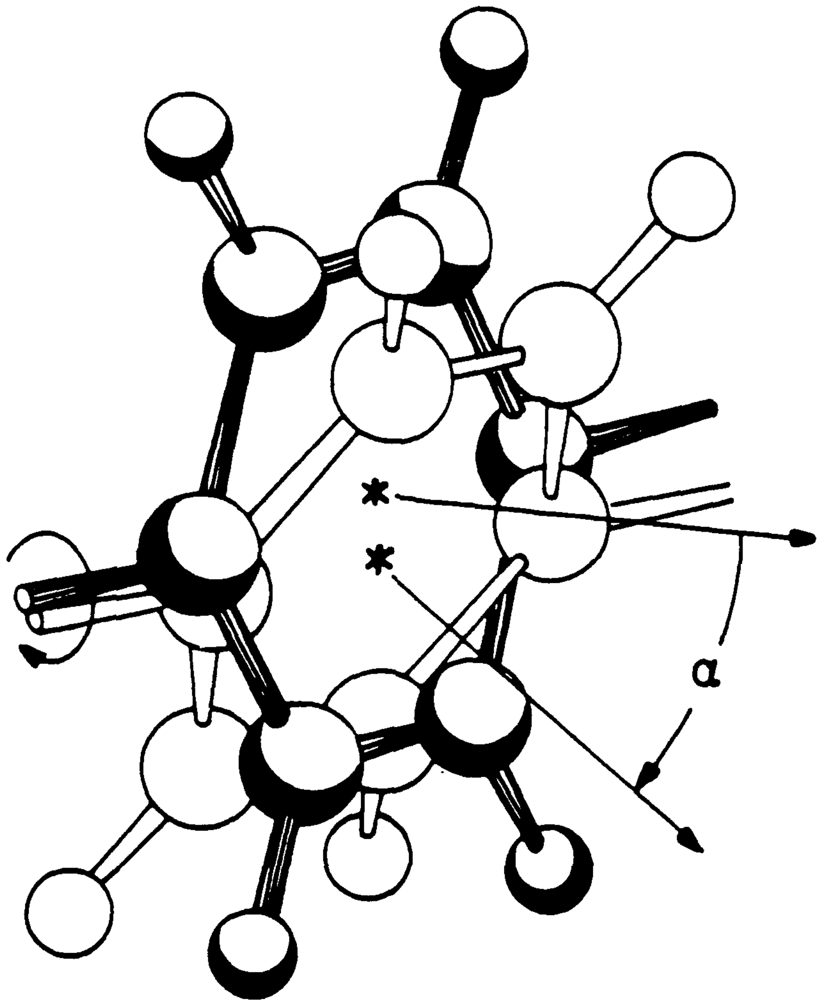


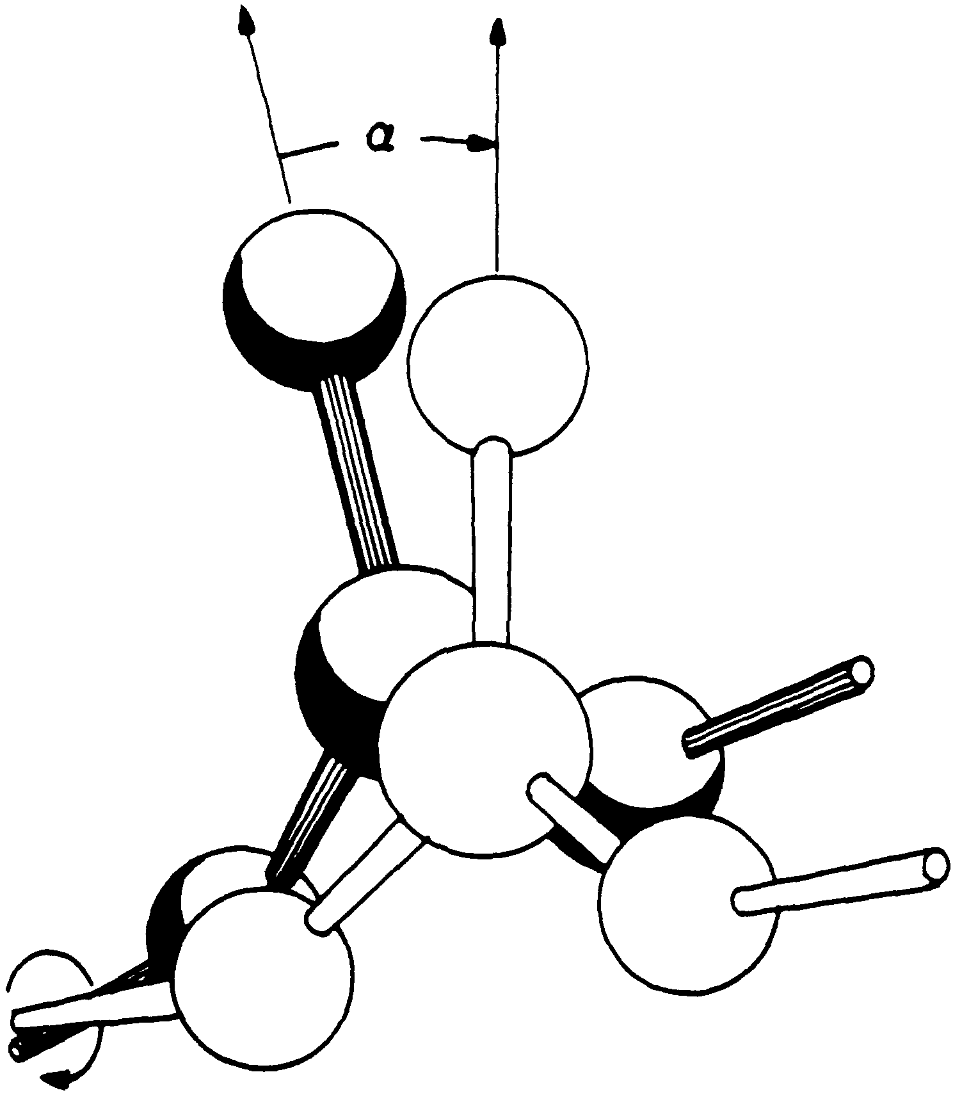
1. PC repeat unit with torsion angles numbered.



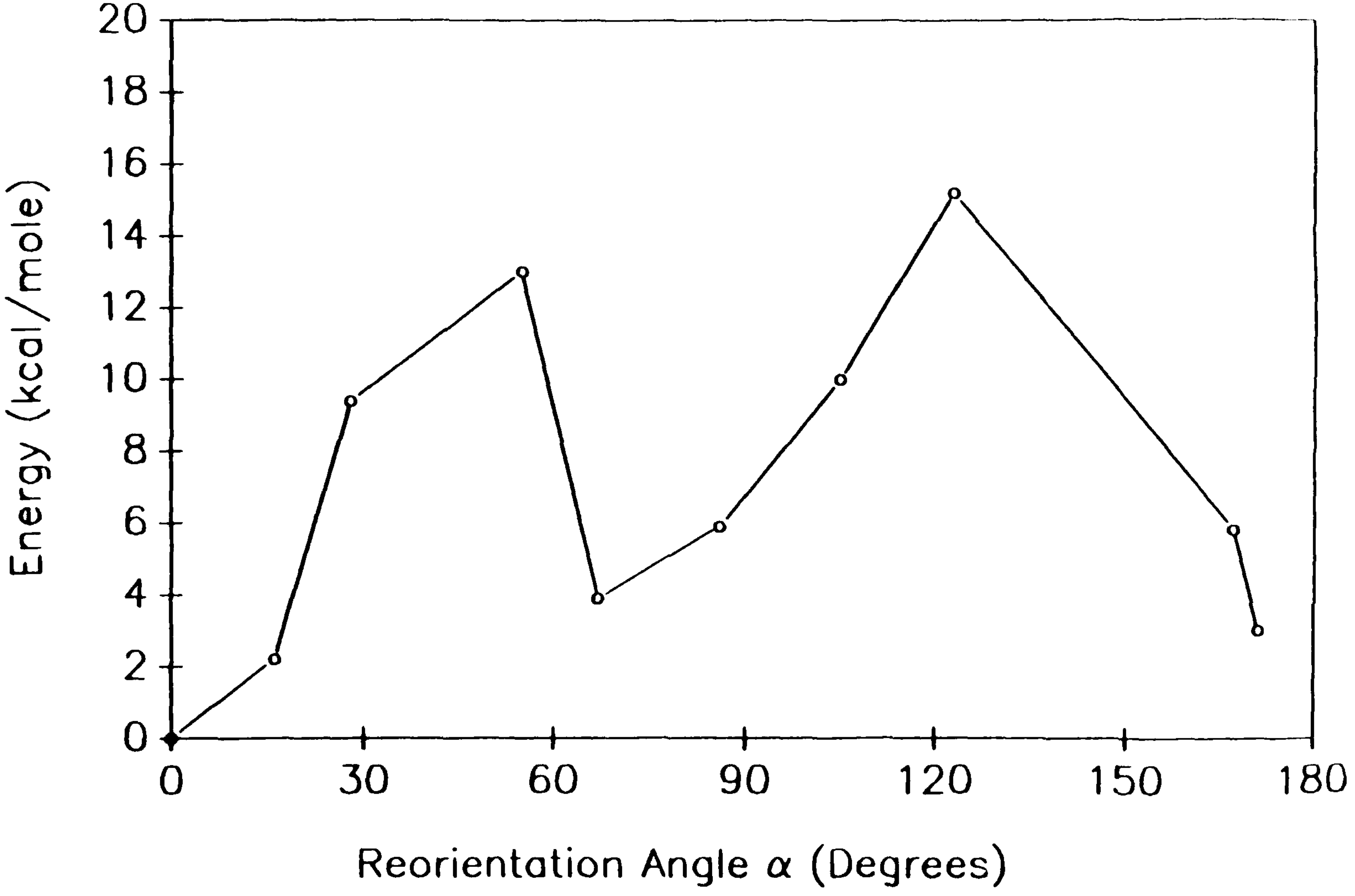
2. Schematic of the simulation technique.



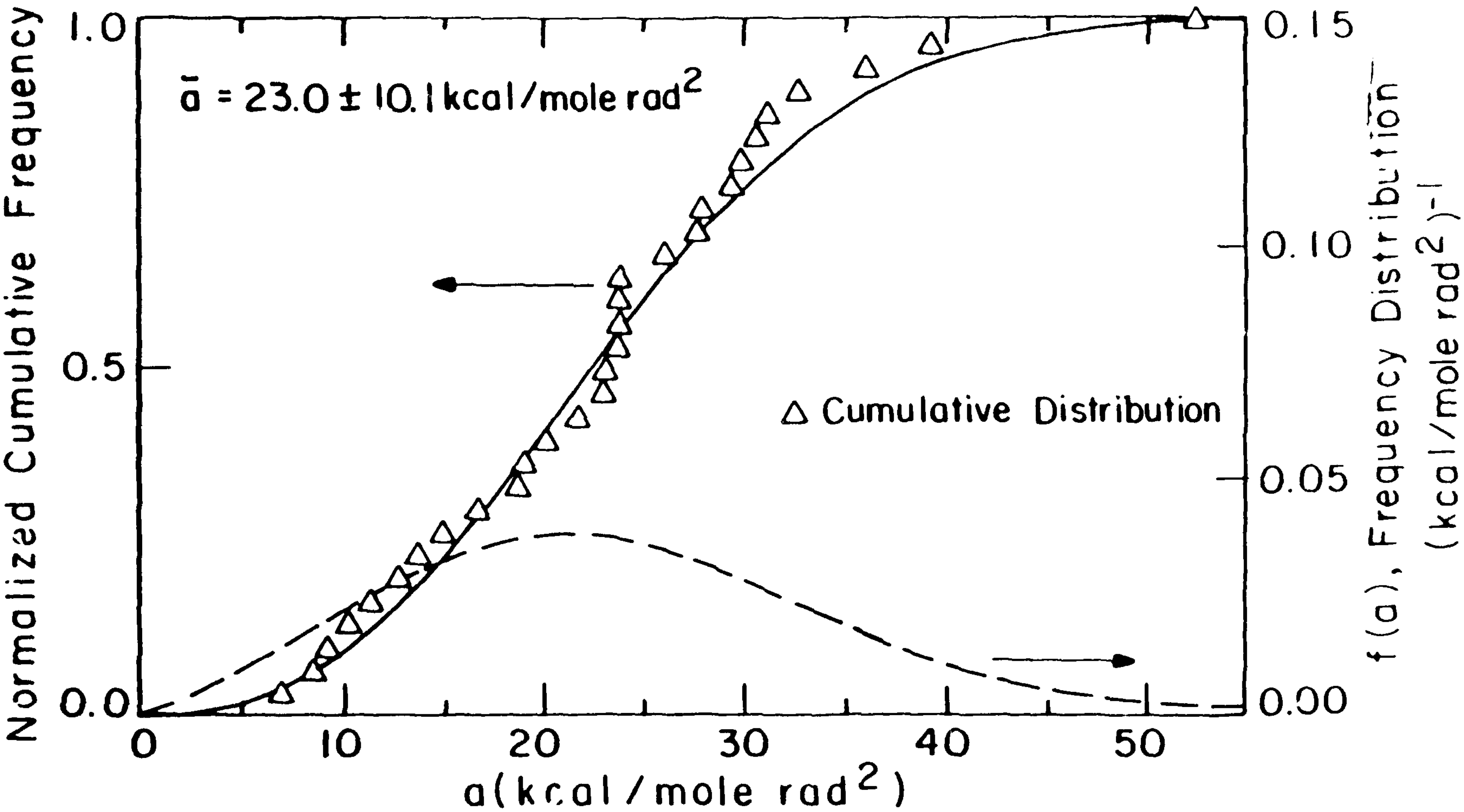
3. Schematic defining the reorientation angle for the ring 'flip' simulation.



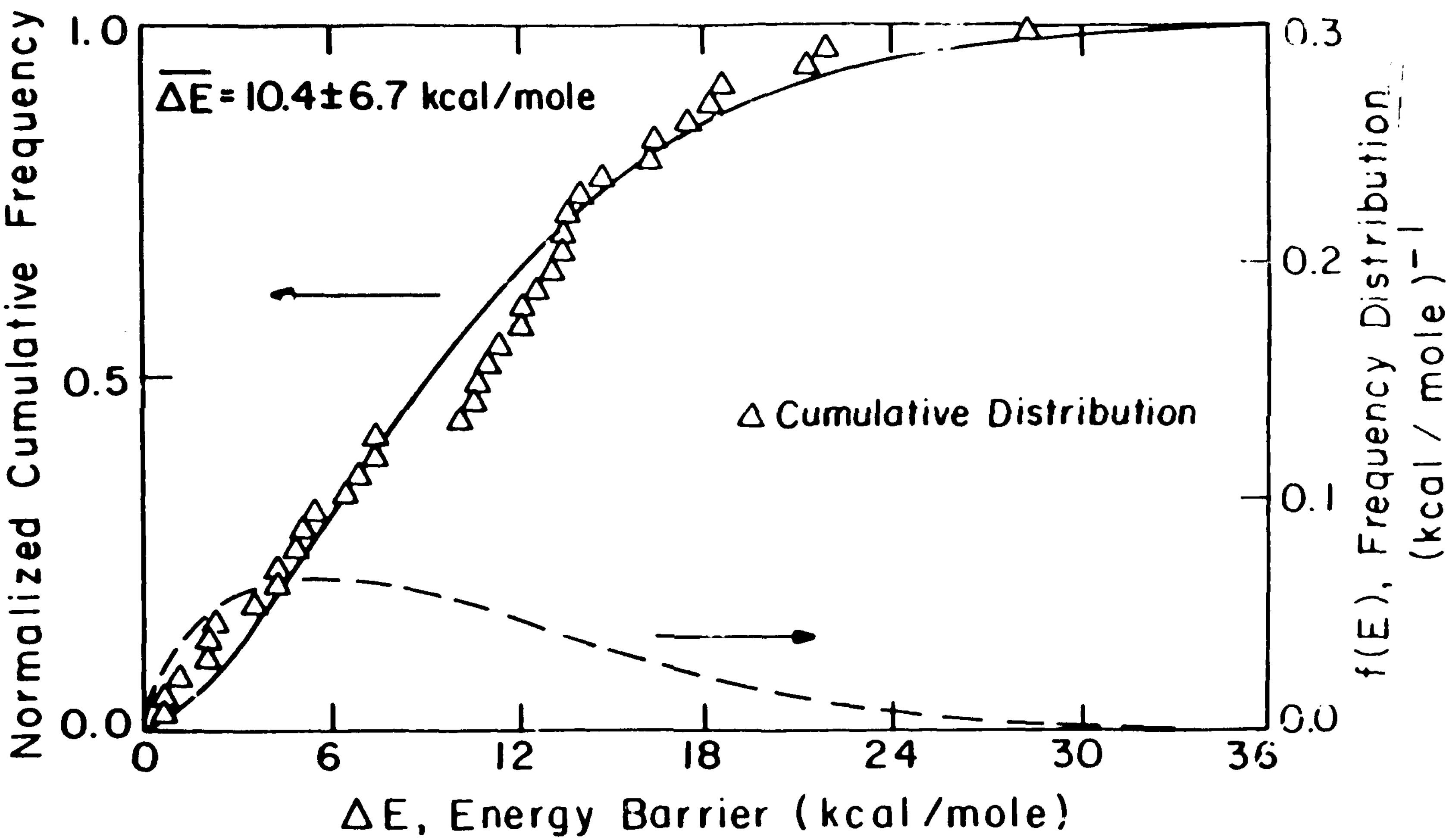
4. Schematic defining the reorientation angle for the carbonate group conformation change simulation.



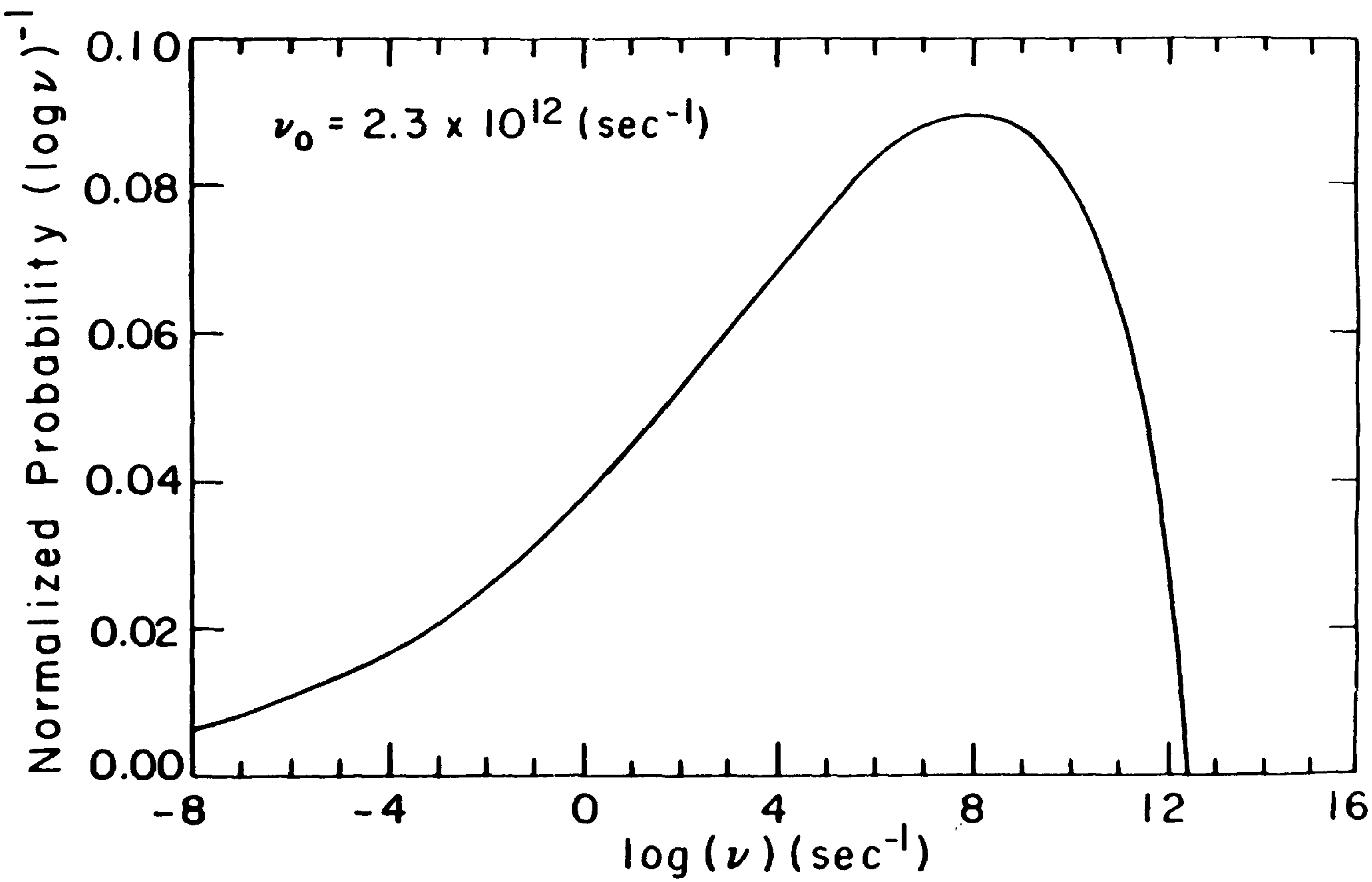
5. Rotational energy path for a ring 'flip' simulation, where increase in system energy vs reorientation angle (defined in Figure 3) is plotted for the third phenylene ring of the chain.



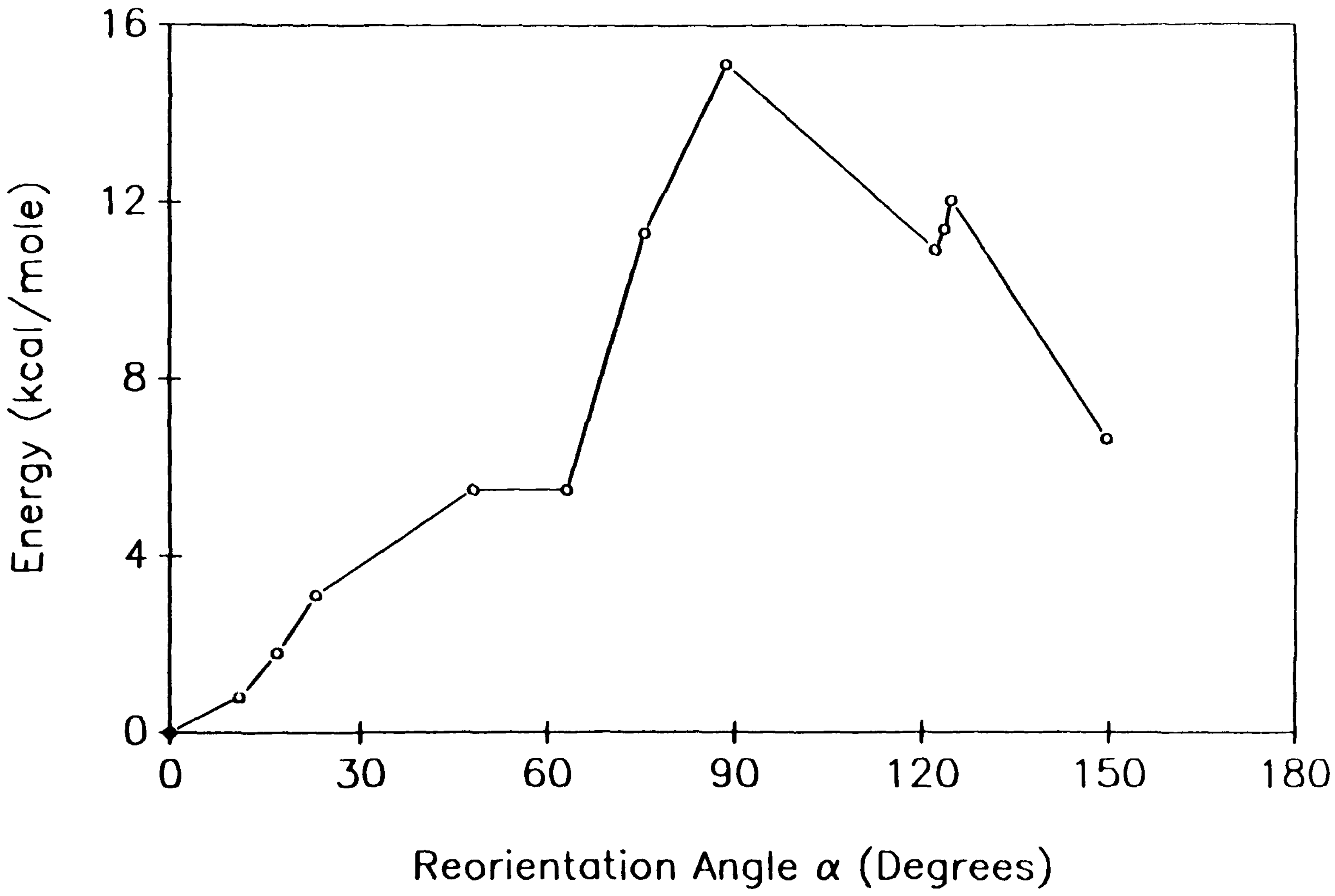
6.) Distribution of curvature coefficient a's for the ring 'flip' simulations, fitted to a Weibull function. The triangles represent the data points, the solid line is the fitted Weibull cumulative distribution, and the dashed line is the fitted Weibull frequency distribution.



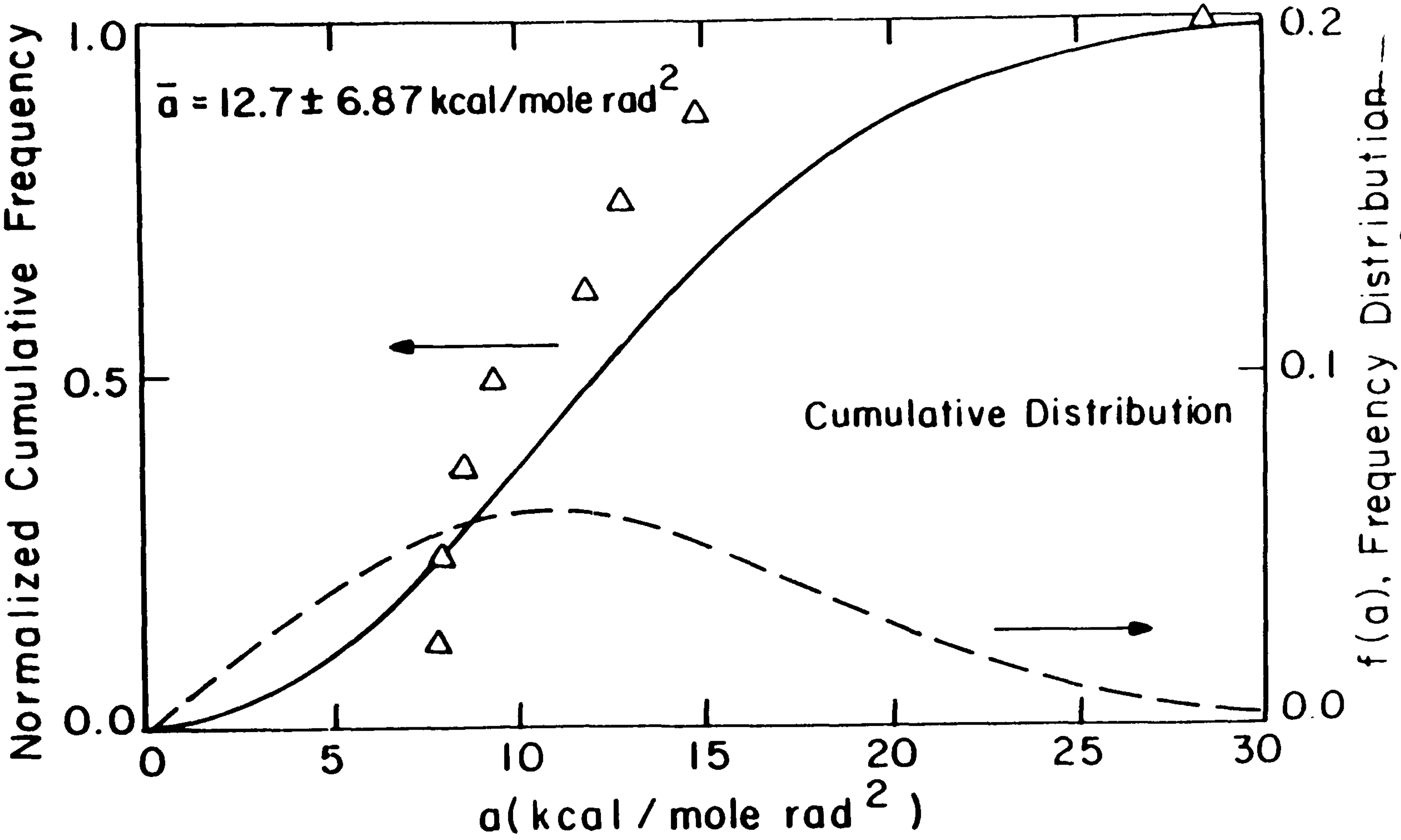
[illegible] Activation energy distribution fitted to a Weibull function for the ring 'flip' simulations. The triangles represent the data points, the solid line is the fitted Weibull cumulative distribution, and the dashed line is the fitted Weibull frequency distribution



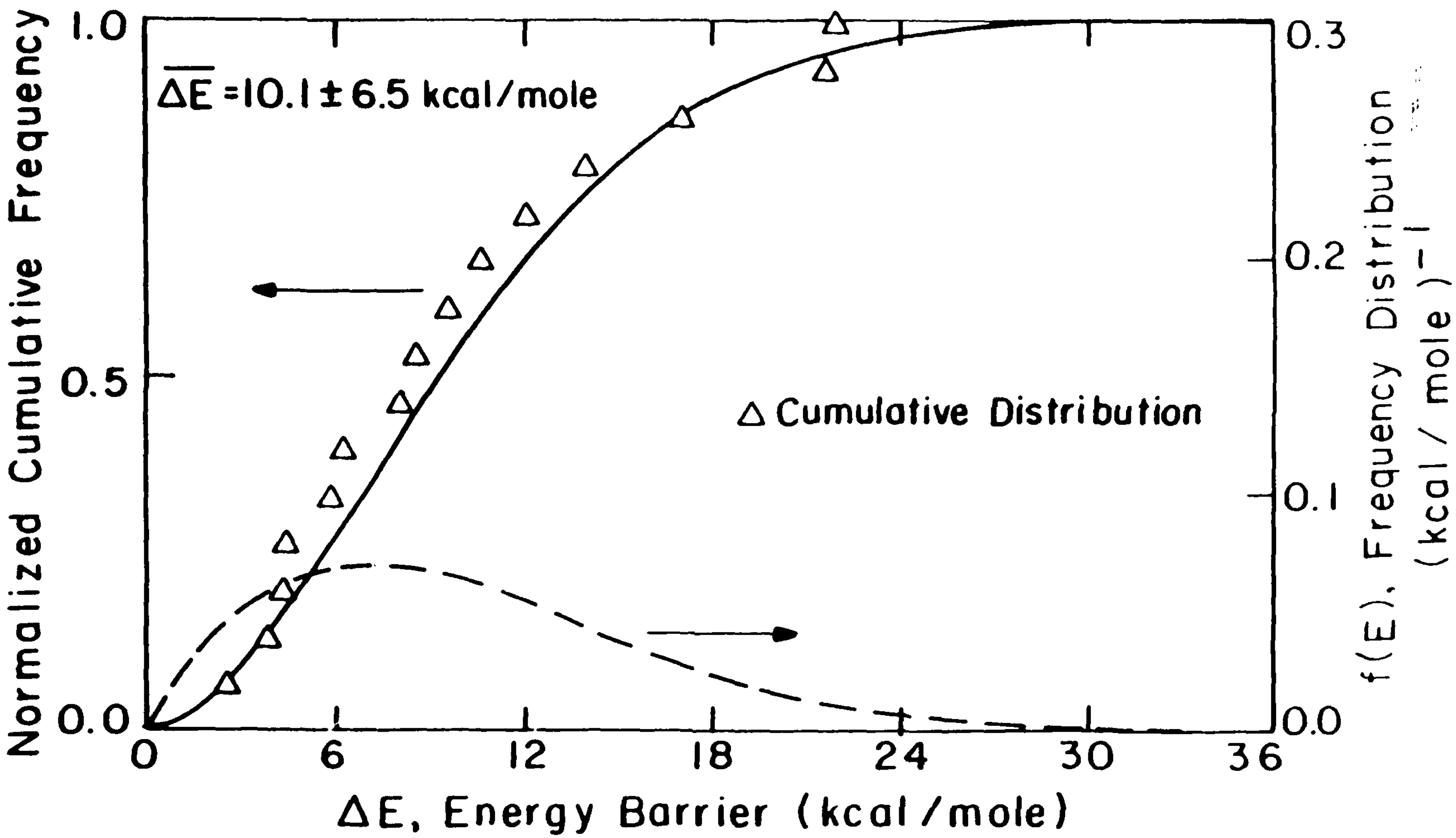
8). Distribution of frequencies for the ring 'flip' simulations.



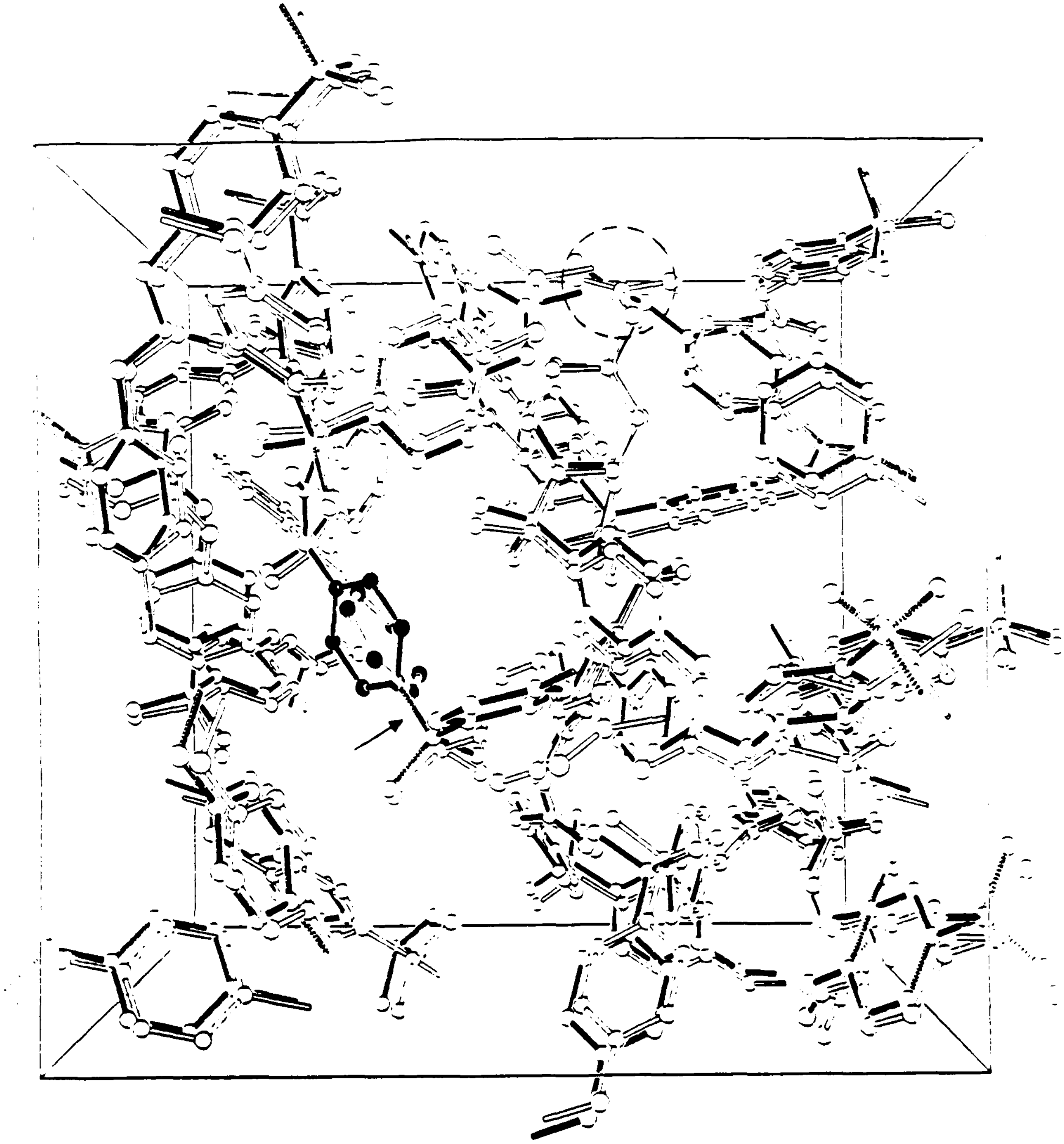
9). Rotational energy path for the conformational changes occurring in the second carbonate group along the chain. The change in the system energy vs. the reorientation angle (defined in Figure 4) is displayed.



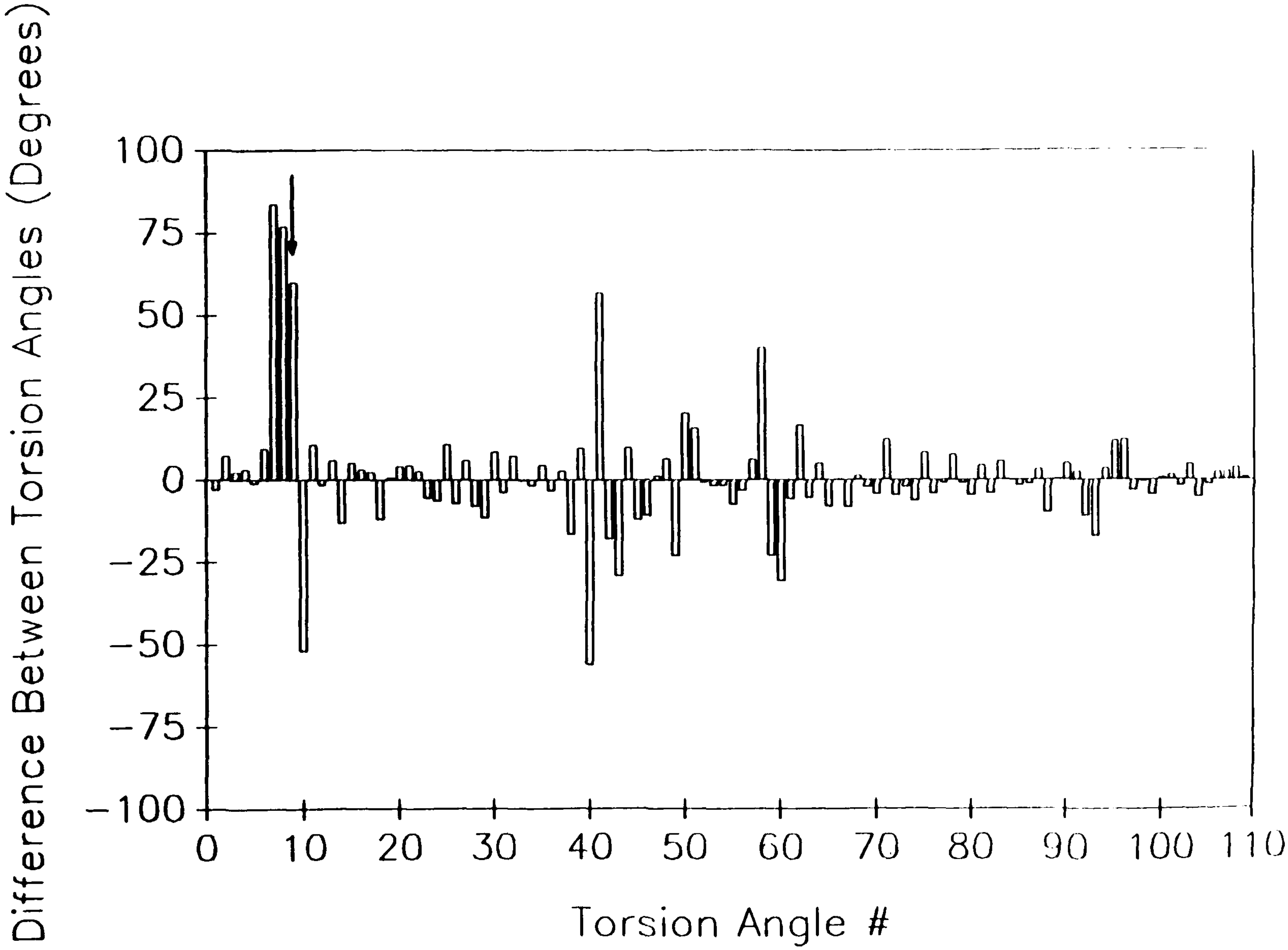
10). Distribution of curvature coefficient *a*'s for the carbonate group conformational change simulations, fitted to a Weibull function. The triangles represent the data points, the solid line is the fitted Weibull cumulative distribution, and the dashed line is the fitted Weibull frequency distribution.



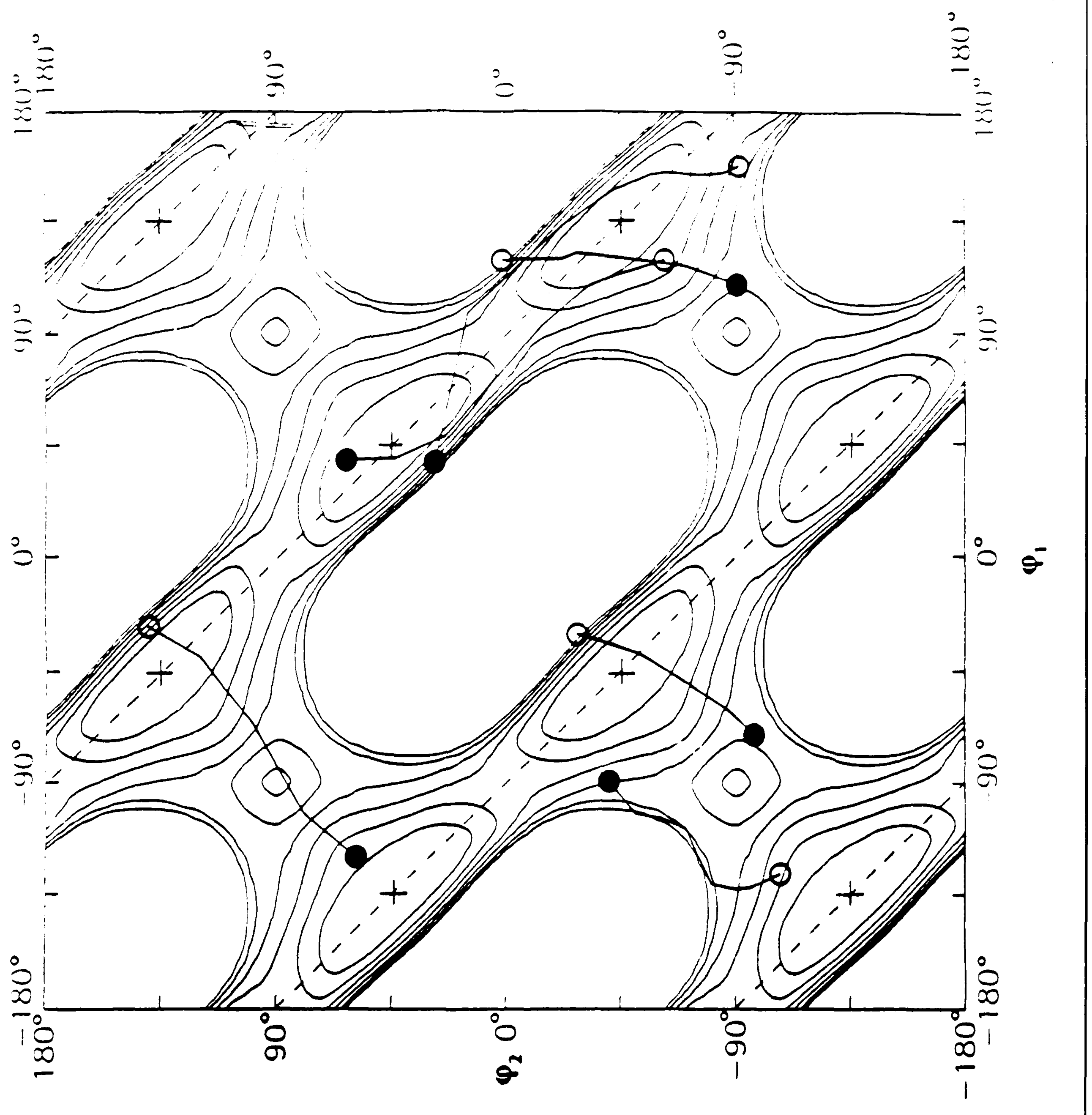
11). Activation energy distribution fitted to a Weibull function for the conformational changes in the carbonate group simulations. The triangles represent the data points, the solid line is the fitted Weibull cumulative distribution, and the dashed line is the fitted Weibull frequency distribution.



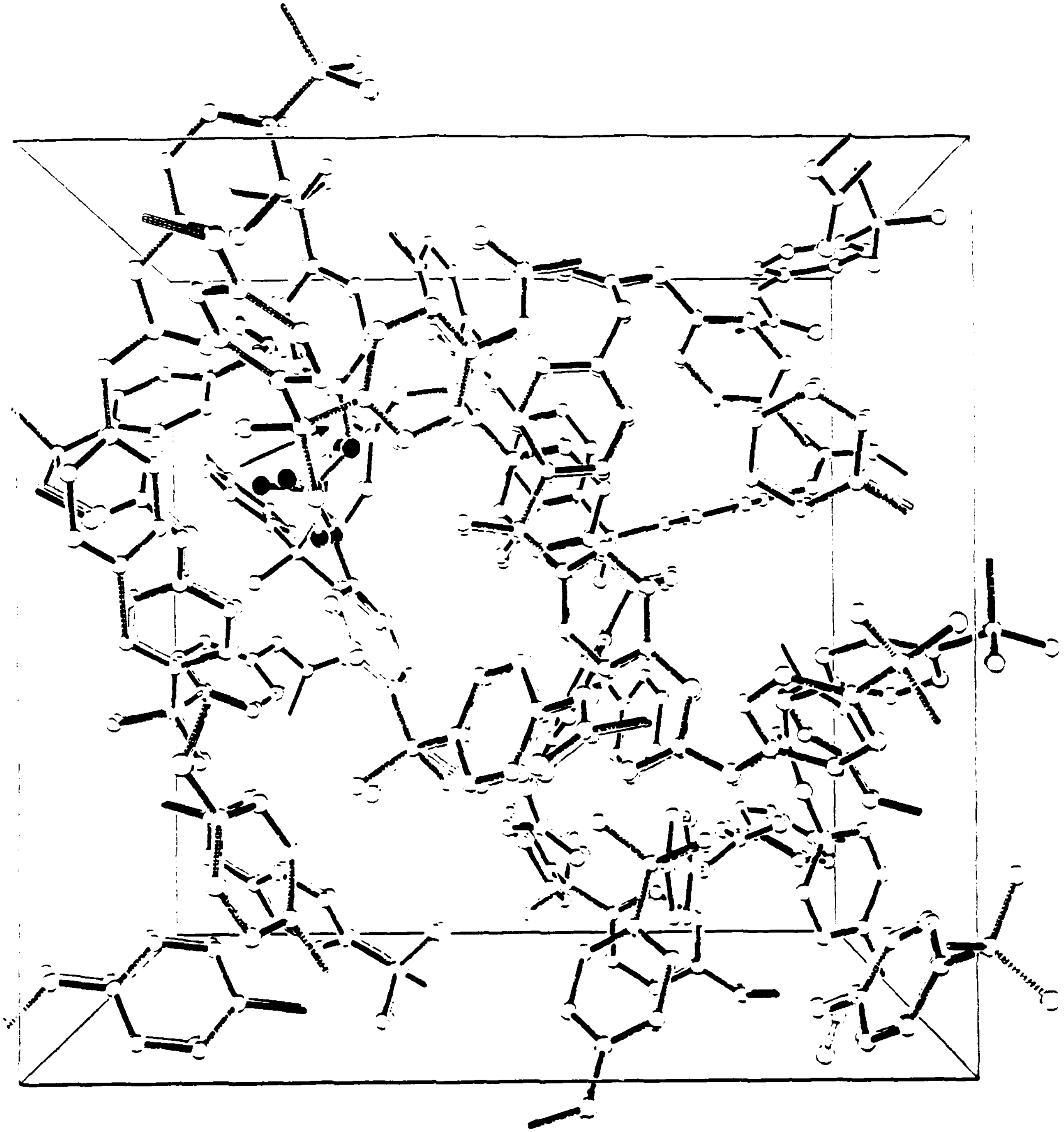
12.) The simulation cube, with hydrogens omitted and atomic radii decreased for clarity. The faint pattern shows the initial configuration of the system ($\alpha = 0^\circ$), while the bold pattern gives the configuration at the peak energy ($\alpha = 55^\circ$) for the simulation where the third phenylene ring along the chain 'flips' (see Figure 5). The phenylene ring that is rotating is shaded black. An arrow identifies the 'driven' torsion angle.



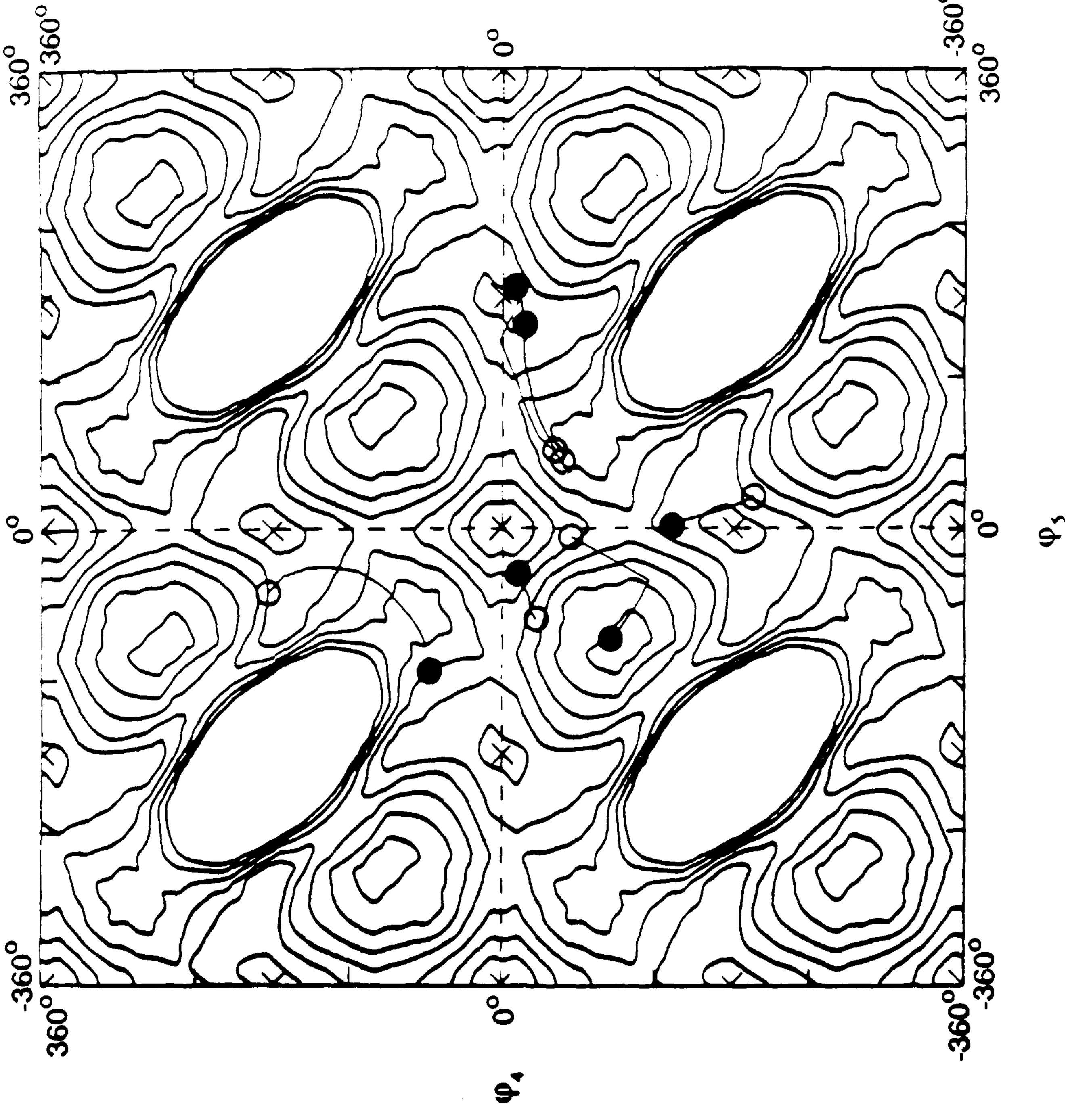
13). The difference between the values of the torsion angles of the chain in the initial configuration (Figure 12, faint pattern) and the conformation of the energy peak (Figure 12, bold pattern) are displayed. The 'driven' torsion angle is φ_9 and is indicated with an arrow.



14). A potential energy contour map of the two torsion angles for 2.2-diphenylpropane which is the local intramolecular energy contribution to the energy barrier and the associated path in configuration space are displayed. The intramolecular minima and energy barrier pathway are, respectively, represented by the × symbols and by the dotted lines. The actual paths taken during several different ring 'flip' simulations, where the end of the path indicated by the empty symbol is the starting position, and the position marked with a filled symbol is the last simulated point, after the energy peaks are superimposed.



15). Figures 15 depict the microstructure at two different points along the rotation path; The faint pattern is the structure at the third point of the rotation path ($\alpha = 23^{\circ}$) and the bold pattern is the structure at the fifth position ($\alpha = 63^{\circ}$) for the simulation where the second carbonate group along the chain changes its conformation (see Figure 9). The carbonate group that is changing conformation is shaded black. An arrow identifies the 'driven' torsion angle.



16). The energy pathways of several simulations where the carbonate group changes conformation are superimposed on a potential energy contour map of the intramolecular interactions that occur in diphenylcarbonate (the torsion angles represented are φ_4 and φ_5 in Figure 1). See caption of Figure 14 for details.