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Equilibrium and Dynamic Conformational Studies on Model Compounds of Side Groups of Polymer Chains with a Potential Capability To Develop Mesomorphic Order[†]

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ABSTRACT: Experimental values of the mean-square dipole moments $\langle \mu^2 \rangle$ are reported for [4-(acetyloxy)phenyl](4-chlorophenyl)methanone (ACM), bis[4-(acetyloxy)phenyl]methanone (BACM), and 4-chlorophenyl 4-(acetyloxy)benzoate (CAB), in the temperature range 30–60 °C. The values of $\langle \mu^2 \rangle$ at 30 °C amount to 16.83, 11.17, and 14.37 D^2 for CAB, ACM, and BACM, respectively. The time evolution of the dipole moment of these compounds and that of [4-(acetyloxy)phenyl]phenylmethanone was followed by molecular dynamics (MD) simulations, and the results for $\langle \mu^2 \rangle$ and $\langle \mu \rangle$ were obtained by averaging these quantities in the whole MD trajectory. In general, good agreement between theory and experiment was found.

Introduction

Thermotropic polymers with mesogenic groups in the main chain exhibit mesophase transitions at high temperatures, rendering the processing of these materials difficult. By separating the mesogenic groups with flexible segments, the thermotropic transition temperatures decrease, facilitating the processing of thermotropic liquid crystalline polymers.[1–4] Studies carried out on thermotropic polyesters prepared from *p,p'*-bibenzoic acid and poly(methylene glycol) (HO–(CH$_2$)$_x$–OH, where x ranges from 5 to 12) show that, by substituting one or more methylene groups by oxygen atoms, bidimensional → tridimensional order transitions occurring in polyesters with polymethylene separators are prevented or at least hindered.[5,6] Differences in conformational characteristics arising from the presence of ether groups in the oxyalkylene separators stabilize the mesophases, on the one hand, and lower the mesophase temperature transitions, on the other.

Another way of obtaining thermotropic polymers lies in attaching the mesogenic entities to polymers as side groups. An important requirement to obtain thermotropic side-chain liquid-crystalline polymers is the placement of a flexible spacer between the mesogenic group and the main chain to partially decouple the mobility of the mesogenic group from that of the main chain.[7–10] However, highly flexible polymers such as polyacrylates, in which the backbone may be significantly distorted, can develop a mesogenic capability even in cases in which the mesogenic groups are directly attached to the backbone.[9] Successful liquid-crystalline formation requires that the mesogenic groups are stiff and contain high-polarizability units such as biphenyl, azobiphenyl, etc. High polarity of the mesogenic groups may enhance both inter- and intramolecular interactions, thus facilitating liquid-crystalline order development.

As part of the studies carried out in our laboratories dealing with the preparation and characterization of new liquid-crystalline polymers based on polyacrylates, in this work attention is given to the study of the polarity and conformational characteristics of model compounds with an apparent capability of developing bidimensional order once attached to the backbone of polymer chains; specifically, the molecules considered are [4-(acetyloxy)phenyl](4-chlorophenyl)methanone (ACM), bis[4-(acetyloxy)phenyl]methanone (BACM), 4-chlorophenyl 4-(acetyloxy)benzoate (CAB), and [4-(acetyloxy)phenyl]phenylmethanone (APM) shown in Figure 1. As a first step, the mean-square dipole moments of the three first compounds were measured, whereas the value of this quantity for APM was taken from an earlier work.[11] By critical interpretation of the experimental results using molecular mechanics, information is obtained concerning the rotational angles, charges distribution, and dynamics of the compounds in real time. This information will be used in further work to study the conformational properties and the capability of developing liquid-crystalline order of acrylate polymers whose side chains have conformational characteristics similar to those of the model compounds described in this work.

Experimental Section

Materials. 4-Chlorophenol (Merck), tetrabutylammonium chloride (Tokio Kasey), and 4-hydroxybenzoic acid (Panamericana SA) were used as received. All analytical-grade solvents and thionyl chloride were distilled prior to use.

4-Chlorophenyl 4-(Acetyloxy)benzoate (CAB). To a refluxing solution of 13.8 g (0.1 mol) of 4-hydroxybenzoic acid and 11.2 g (0.1 mol) of 4-chlorophenol in 200 mL of dioxane was added dropwise 11.8 g (0.1 mol) of thionyl chloride. The reflux was maintained for 5 h and then it was poured into 1 L of cool water. The precipitate was filtered, dried, and recrystallized three times from xylene. The yield of the compound thus obtained, 4-chlorophenyl 4-hydroxybenzoate (CHB), was 14.3 g (57.5%). 4-Chlorophenyl 4-(acetyloxy)benzoate was obtained by reacting CHB with acetic anhydride in an alkaline aqueous medium; the product was purified by chromatography

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[†] This paper is dedicated to Professor Eloisa B. Mano on the occasion of her 70th birthday.

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in a basic aluminum oxide bead using dichloromethane as eluent, and then it was recrystallized from tetrachloromethane. Yield: 84%. Mp: 124.6 °C. ^{13}C-NMR ($CDCl_3$): δ 21.3 (CH_3-); 122.0, 123.2, 129.7, 132.0, 132.1, 132.2, 149.5, 155.2 (C^{ar}); 164.3 ($-ArCOOAr-$); 168.9 (CH_3COO-). (The NMR spectra of CAB and BACM were registered with a Bruker AM 200 apparatus, whereas that of ACM was recorded with a Varian XL-300. In all the cases TMS was used as internal reference.)

[4-(Acetyloxy)phenyl](4-chlorophenyl)methanone (ACM). A suspension of 24.8 g (0.158 mol) of 4-chlorobenzoic acid (I) and 35.7 g (0.3 mol) of thionyl chloride in 300 mL of dry xylene was refluxed for ca. 6 h until complete solubilization was achieved. The solution was fractionated by distillation until the temperature at the top of the column reached 135 °C. The remaining solution was dropwise added to an aqueous cooled solution of 18.8 g (0.2 mol) of phenol, 8.0 g (0.2 mol) of sodium hydroxide, and 1 g of tetrabutylammonium chloride, under strong stirring. The organic layer was evaporated, and the residue was recrystallized from isooctane. The yield of the compound thus obtained, 4-chlorophenylbenzoate (**II**), was 27.4 g (74%). A total of 26.7 g (0.2 mol) of aluminum chloride was quickly added to 22 g (0.094 mol) of **II**, and after 5 min of reaction the mixture was poured into an equal mixture of ice and 6 N HCl. The resulting mixture was slowly heated until complete neutralization of the inorganic compounds. The waxy residue was dissolved in hot toluene and then extracted with 200 mL of 2 N NaOH. The aqueous layer was treated with activated charcoal, filtered, and acidulated with 6 N HCl. The precipitate, (4-chlorophenyl)(4-hydroxyphenyl)methanone (**III**), was recrystallized from methanol and dried in a vacuum oven at 60 °C. Yield: 14.2 g (41.3%). [4-(Acetyloxy)phenyl](4-chlorophenyl)methanone (ACM) was synthesized by reacting 1 g of **III** with acetic anhydride in an alkaline medium. The product ACM was separated by chromatography using a basic aluminum oxide bead and dichloromethane as eluent; finally it was recrystallized from toluene/hexane (1:1). Yield: 0.9 g (76.2%). Mp: 126 °C. ^{13}C-NMR ($CDCl_3$): δ 20.1 (CH_3-); 120.6, 127.7, 130.3, 130.4 ($C^{ar}H$); 133.8, 134.9, 138.0, 153.1 ($C^{ar}-$); 167.7 ($-COO-$); 193.1 ($-CO-$).

Bis[4-(acetyloxy)phenyl]methanone (BACM). To a refluxing solution of 13.8 g (0.1 mol) of 4-hydroxybenzoic acid and 18.8 (0.2 mol) of phenol in 200 mL of dioxane was added dropwise 11.8 g (0.1 mol) of thionyl chloride. The reflux was maintained for 5 h, then the reaction products were poured into cool water, and the precipitate, phenyl 4-hydroxybenzoate (**IV**), was filtered, dried, and recrystallized three times from xylene. Yield: 11.0 g (51.0%). A solution of 13.3 g (0.1 mol) of aluminum chloride and 10 g (0.046 mol) of **IV** in 100 mL of dry nitrobenzene was stirred for 12 h at room temperature and heated at 100 °C for 2 h more. The solution was smoothly poured into an equal mixture of ice and 6 N HCl, and before achieving complete neutralization and solubilization of the inorganic compounds, 100 mL of xylene was added. The organic layer was extracted with 100 mL of 2 N NaOH. The aqueous layer was treated with activated charcoal, filtered, and acidulated with 6 N HCl. The precipitate was twice recrystallized from ethyl acetate/hexane (2:1) and dried in a vacuum oven at 60 °C. Yield: 5.2 g (52%). The product obtained, bis(4-hydroxyphenyl)methanone, was treated with acetic anhydride in an aqueous medium and purified in the same way as CAB. Yield of BACM; 50.3%. Mp: 155.6 °C. ^{13}C-NMR ($CDCl_3$): δ 20.1 (CH_3-); 120.6, 130.5 ($C^{ar}H$); 134.0 (C^{ar}-CO$-$); 152.9 ($C^{ar}OCO-$); 167.8 ($-COO-$); 193.2 ($-CO-$).

Dielectric Measurements. The dielectric permittivity ϵ of solutions of the compounds were measured at different temperatures in benzene with a capacitance bridge (General Radio, type 1620A) and a three-terminal cell; the measurements were performed at 10 kHz. Increments in the index of refraction of the solutions with respect to the solvent were obtained at the temperatures of interest with a Brice–Phoenix differential refractometer.

Table 1. Summary of Dielectric Results for 4-Chlorophenyl 4-(Acetyloxy)benzoate (CAB), [4-(Acetyloxy)phenyl](4-chlorophenyl)methanone (ACM), and Bis[4-(acetyloxy)phenyl]methanone (BACM)

molecule	T, °C	$2n_1$, dn/dw	dϵ/dw	$\langle\mu^2\rangle$, D^2
CAB	30	−0.107	6.018	16.83
	40	−0.086	5.848	17.21
	50	−0.065	5.602	17.35
	60	−0.043	5.415	17.62
ACM	30	0.154	4.455	11.17
	40	0.211	4.274	11.14
	50	0.213	4.122	11.31
	60	0.216	4.014	11.59
BACM	30	0.092	5.191	14.37
	40	0.110	5.055	14.71
	50	0.129	4.889	14.95
	60	0.147	4.756	15.26

Experimental Results

Values of the mean-square dipole moments $\langle\mu^2\rangle$ of the model compounds were determined at different temperatures by using the relations of Guggenheim–Smith[12,13]

$$\langle\mu^2\rangle = \frac{27k_BTM}{4\pi\varrho N_A(\epsilon_1 + 2)^2}\left\{\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right\} \qquad (1)$$

where N_A and k_B are respectively Avogadro's number and the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, and ϱ and ϵ_1 are respectively the density and dielectric permittivity of the solvent. Values of dϵ/dw in the limit $w \to 0$, where w is the weight fraction of polymer, were obtained from the plots of the dielectric permittivity of the solution, ϵ, *vs* w. The results obtained at different temperatures are indicated in the fourth column of Table 1. The term dn/dw in eq 1 was determined from the slopes of the plots of the increments of the index of refraction of the solution with respect to that of the solvent ($\Delta n = n - n_1$) against w. The corresponding results for $2n_1$ dn/dw are given in the third column of Table 1. Values of $\langle\mu^2\rangle$ for the compounds at different temperatures, with an uncertainty of ±3%, are shown in the fifth column of this table.

Values of the temperature coefficient of the mean-square dipole moment of the model compounds, expressed as 10^3 d ln $\langle\mu^2\rangle$/dT, amounted to 1.2, 1.9, and 1.4 K^{-1} respectively for ACM, BACM, and CAB.

Theoretical Results and Discussion

Figure 1 (a–d) shows the structure of the four molecules studied in their planar *all-trans* conformations for which all the rotational angles are taken to be 180°. Rotations that define the conformation of the molecules are labeled ϕ_1, ϕ_1', ϕ_2, and ϕ_3. Approximate locations of the main contributions for the dipole moment of each molecule are represented by arrows pointing from negative to positive centers of charge. The modules of these contributions can be obtained from the experimental dipole moments of model compounds in solution.[14] Thus, values of μ_1 = 1.7 D (experimental value measured for phenyl acetate), μ_2 = 3.0 D (average of experimental values obtained for benzophenone), μ_3 = 1.6 D (from chlorobenzene), and μ_4 = 1.9 D (from phenyl benzoate) are found in the literature. The direction of the dipole moment of ester groups form an angle $\tau \approx 123°$ with the direction of the CH_3-C^* bond,[15] while the dipole moment, μ_2 representing the ketone group lies very close to the direction of the $O=C^*$ bond.

The dipole moment information contained in Figure 1 is only approximate, and it is shown just with

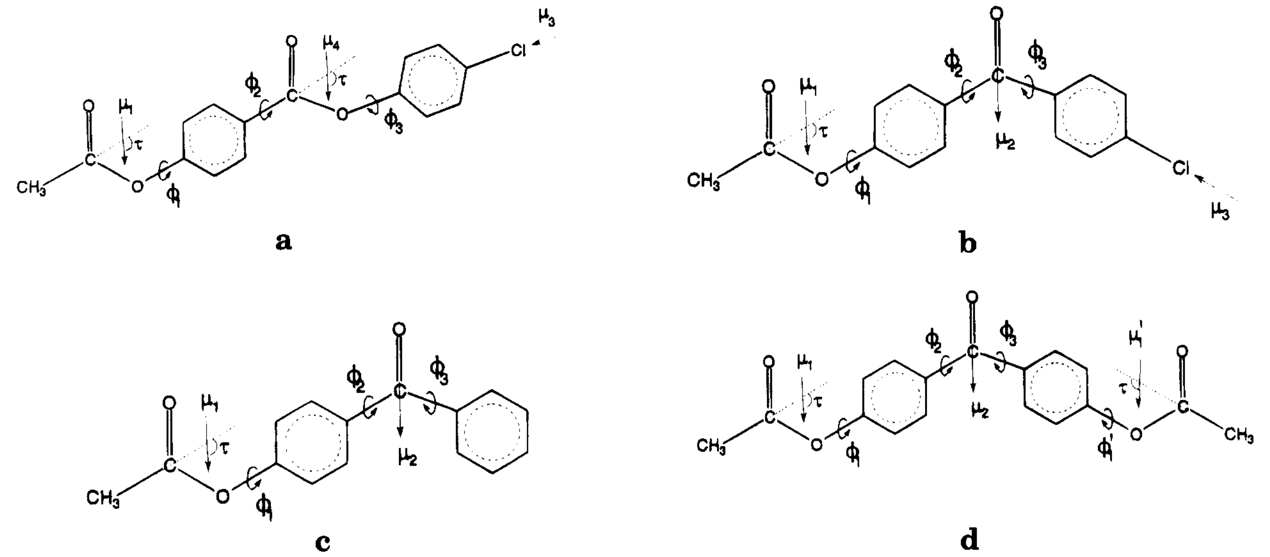

Figure 1. Schematical representation of the four molecules studied in the present work shown in their planar *all-trans* conformation for which the value $\phi_i = 180°$ was assigned to all the rotational angles. Arrows pointing from negative to positive centers of charge indicate the approximate direction of the contributions to the total dipole moment of each molecule. 4-Chlorophenyl 4-(acetyloxy)benzoate (CAB) (a), [4-(acetyloxy)phenyl](4-chlorophenyl)methanone (ACM) (b), [4-(acetyloxy)phenyl]-phenylmethanone (APM) (c), and bis[4-(acetyloxy)phenyl]methanone (BACM) (d).

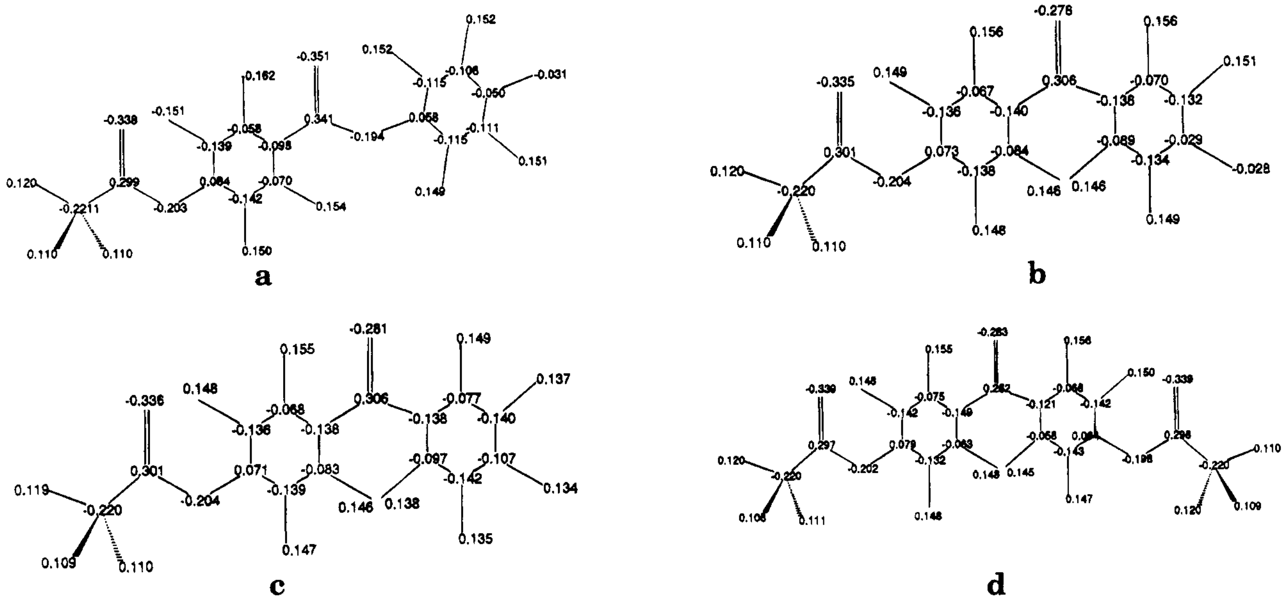

Figure 2. Partial charges (in electronic units of charge) assigned to each atom of the four molecules: 4-chlorophenyl 4-(acetyloxy)-benzoate (CAB) (a), [4-(acetyloxy)phenyl](4-chlorophenyl)methanone (ACM) (b), [4-(acetyloxy)phenyl]phenylmethanone (APM) (c), and bis[4-(acetyloxy)phenyl]methanone (BACM) (d). These charges were used for all the calculations presented in this work. See text for details.

illustrative purposes. The actual calculation of dipole moments of each molecule was performed by assigning partial charges to all the atoms in the molecule and computing the center of positive and negative charges for each conformation that the molecule adopts during the simulation. This procedure loses the intuitive aspects of adding vector contributions (something that we try to keep in part with the arrows on Figure 1), but it has the advantage of taking into account the variation of the dipole moments associated with bond length oscillations produced along the simulation. The partial charges were computed with the Sybyl molecular modeling package[16] employing the AMPAC program and the AM1 procedure.[17,18] The charges assigned to each atom are indicated in Figure 2.

Molecular dynamics (MD) simulations for the compounds in the gaseous state were carried out with Sybyl,[16] using the Tripos force field.[19] In the evaluation of the Coulombic contributions to the potential energy, the dielectric permittivity was considered, as usual, to be 4. The geometry of each molecule was first optimized with respect to all bond lengths, bond angles, and rotations, and the resulting conformation was used as the starting point for the MD trajectory in which the Verlet algorithm[20] was employed to integrate the Newton equation of motion for each atom with a given value of time step δ. All our calculations were carried out using a time step $\delta = 1$ fs (10^{-15} s). The molecule was first warmed up from 0 K to the working temperature of 300 K with increments of 20 K and allowing a relaxation period of 500 time steps in each intermediate temperature. Once the working temperature was reached, the simulation was continued for 2×10^6 time steps (i.e., during 2 ns) at constant temperature, and the data of interest (i.e., geometry, energy, and dipole moment) were recorded every 500 fs.

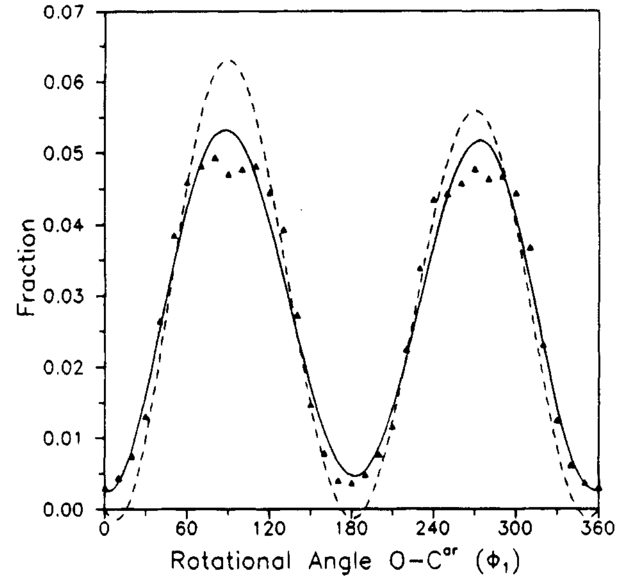

Figure 3. Distribution of probabilities for the rotations around O−C^{ar} bonds such as ϕ_1 and ϕ_1'.

Figure 3 shows the probability distribution of rotational angle ϕ_1 (or ϕ_1') in the phenyl acetate residue. The results of all the molecules are almost identical as far as this rotation is concerned. The triangles in Figure 3 indicate the actual results of the MD simulation computed as the fraction of conformations in which the value of ϕ_1 lies within an interval of 10° (for instance, the probability for $\phi_1 = 20°$ is computed counting the fraction of conformations having $15 < \phi_1 < 25°$). The solid line on this figure represents a least-squares fitting of the results to a polynomial of the 9th degree which is used to smooth the results. Finally, the broken line shows the results obtained with an energy calculation performed moving ϕ_1 from 0 to 350° with 10° increments, and minimizing the energy with respect to all other variables, these energies were transformed into Boltzmann factors, normalized to give a sum of unity, and fitted to a 9th degree polynomial which is represented by the broken line. As Figure 3 shows, there is excellent agreement between the results obtained by MD simulation and energy calculations, both of them indicating the presence of two minima for the conformations in which the plane of the ester is roughly perpendicular to that of the phenyl ring, i.e., $\phi \approx 90, 270°$. The difference in height of the two peaks on the broken line is obviously a fallacy of the calculation since the symmetry of the molecule requires that both conformations have the same energy while the calculations produce differences of ca. 0.08 kcal mol^{-1} among them due to imperfect minimization.

Rotations ϕ_2 and ϕ_3 for the ketone group (i.e., rotations C^{ar}C^{ar}−C*C^{ar}) are equivalent in the three ketones studied. The probability distribution for these rotations is shown in Figure 4 which indicates the presence of two maxima around 0 and 180°, i.e., when the ketone group is roughly coplanar with the phenyl ring.

The probability for the pair of rotations ϕ_2 and ϕ_3 is represented, both as 2D and 3D plots, in Figure 5 for the ketone derivatives (compounds ACM, APM, and BACM) and Figure 6 for the ester (molecule CAB). In the case of ketones (Figure 5), the most important feature is that the maxima of probability are not located at the combination of maxima of the two rotational angles when taken separately, but they are separated by ca. 30° from those positions. Thus, the maxima in Figure 5 are not $\phi_2, \phi_3 = 0°, 180°$ but $\phi_2, \phi_3 = 0 \pm 30°, 180 \pm 30°$ with displacement of the same sign in both rotational angles; i.e., $\phi_2 = \phi_3 \approx \pm 30°$ are maxima of probability, while $\phi_2 = 30°, \phi_3 = -30°$ or $\phi_2 = -30°, \phi_3 = 30°$ has very little probability due to interactions between the H in the ortho position in the phenyl groups. However, in the case of the ester (Figure 6), rotations ϕ_2 and ϕ_3 are almost uncorrelated and the maxima of probability are located close to the positions $\phi_2 = 0°, 180°, \phi_3 = 90°, 270°$.

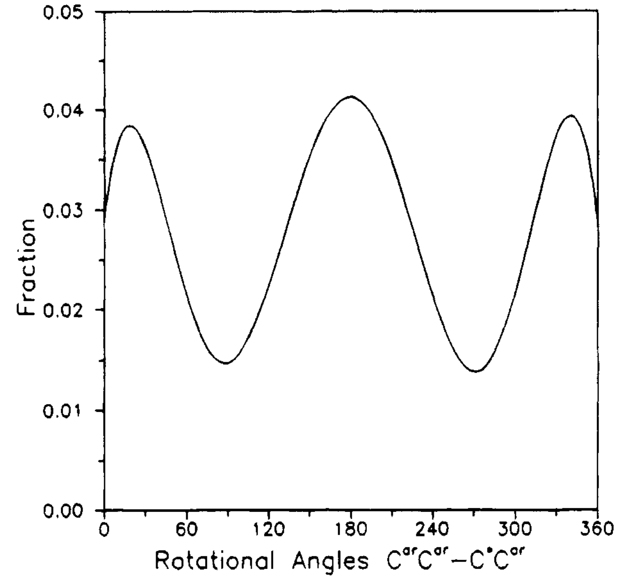

Figure 4. Distribution of probabilities for rotations around C^{ar}C^{ar}−C*C^{ar} bonds such as ϕ_2 and ϕ_3 in [4-(acetyloxy)phenyl]-(4-chlorophenyl)methanone (ACM), [4-(acetyloxy)phenyl]-phenylmethanone (APM), and bis[4-(acetyloxy)phenyl]methanone (BACM).

The evolution of the dipole moment of each molecule with time is shown in Figure 7 which represents the dipole moment of the conformations adopted by the molecule during the MD simulation. Values of $\langle\mu\rangle$ and $\langle\mu^2\rangle$ averaged over the whole MD trajectory are summarized in Table 2 together with the experimental results of this last magnitude. In general, the agreement between theory and experience is very good, with the only exception of BACM for which the theoretical value is ca. 19% larger than the experimental one. However, as will be explained below, the accuracy in the calculation for this molecule is much worse than in any of the other three.

Although the actual calculation of μ for each conformation was performed using the partial charges of Figure 2, the qualitative analysis of the results can be presented in a more intuitive fashion by employing the approximate contributions indicated in Figure 1.

Let us start with compound APM whose results can be explained in a more straightforward way. As Figure 1c indicates, this molecule contains two contributions to the dipole moment: $\mu_1 \approx 1.7$ D from the ester group and $\mu_2 \approx 3$ D from the ketone. Thus, conformations in which both contributions are parallel would give[21] $\mu \approx 4.7$ D, while if the two contributions are antiparallel, the total dipole moment of the molecule should be close to 1.3 D. Figure 7c shows that the conformational changes occur rather quickly and the molecule passes from high to low polar conformations in times smaller that 0.1 ns, although the conformations more frequently adopted have $\mu \approx 2.5-4.0$ D and the value of $\langle\mu\rangle$ averaged over all the conformations is 3.33 as is

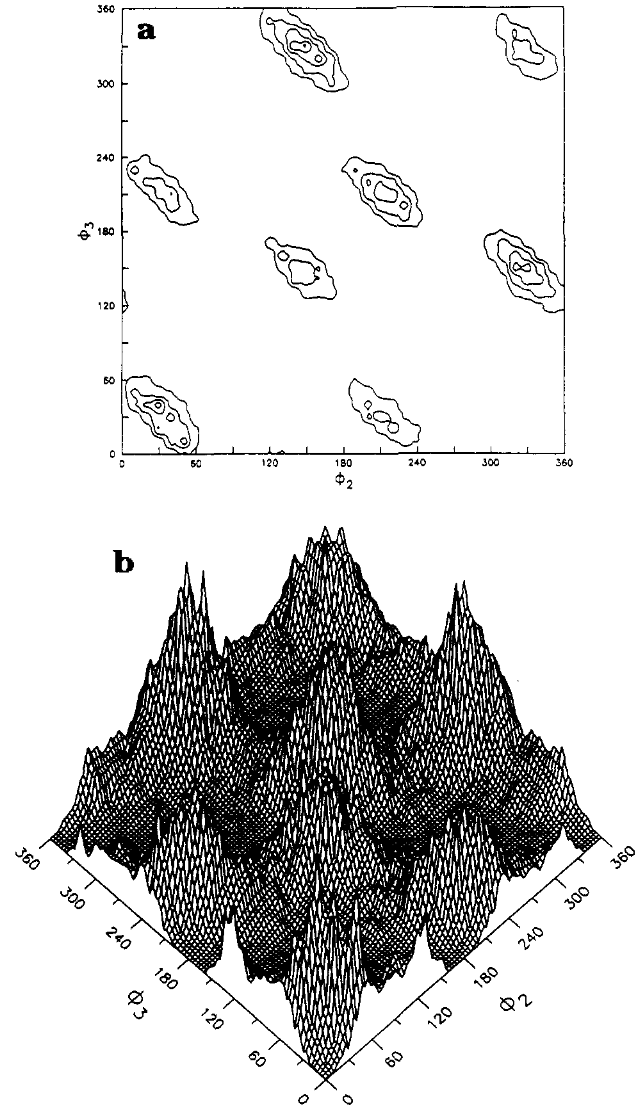

Figure 5. Distribution of probabilities, in 2D (a) and 3D (b) representations, for simultaneous rotations around the pair of bonds $C^{ar}C^{ar}-C^*-C^{ar}C^{ar}$ in the ketone residue (ϕ_2 and ϕ_3 rotational angles in [4-(acetyloxy)phenyl](4-chlorophenyl)-methanone (ACM), [4-(acetyloxy)phenyl]phenylmethanone (APM), and bis[4-(acetyloxy)phenyl]methanone (BACM).

indicated in Table 2. The amount of time that the molecule expends in either high or low polarity conformations is roughly the same according to the results shown in Figure 7c. In other words, the probability of having reinforcement or cancelation among the μ_1 and μ_2 contributions is about the same, both contributions are practically uncorrelated, and the average $\langle\mu^2\rangle$ is almost identical to the value nm^2.

The analysis of BACM is also very simple. According to Figure 1, this molecule could be schematically obtained by adding a second ester group, and therefore a second contribution μ_1' to molecule ACM. The maximum value of μ for BACM will then be[21] $\mu \approx 2\mu_1 + \mu_2 \approx$ 6.4 D, while the three contributions could, in principle, completely cancel each other out, giving a minimum value of μ close to zero. The orientation of this new contribution μ_1' is governed by the rotational angles ϕ_1' and ϕ_2 so that, for each set of values of ϕ_1, ϕ_2 (that in the case of APM would completely define the dipole moment of one conformation), in the case of BACM, ϕ_1' and ϕ_2 rotations would allow the μ_1' contribution to either add or to subtract from the resulting $\mu_1 + \mu_2$. The effect is like allowing each point of Figure 7c the possibility of changing the result of μ by a number in the range ±1.7 D, thus increasing the limits of oscillation, as is in fact obtained in Figure 7d. Averaged values $\langle\mu\rangle = 3.93$ D and $\langle\mu^2\rangle = 16.9$ D^2 are obtained from Figure 7d. This last result is larger than the value nm^2 = 14.8 D^2 that would be obtained with uncorrelated contributions, while according to Table 2 the experimental result 14.3 D^2 is almost identical to the uncorrelated value. Inspection of Figure 7d and comparison with parts a–c show very clearly that the accuracy on the average $\langle\mu\rangle$, and even more on $\langle\mu^2\rangle$ where the oscillations have a much larger effect, should be much smaller in the molecule BACM than in all the other molecules studied here.

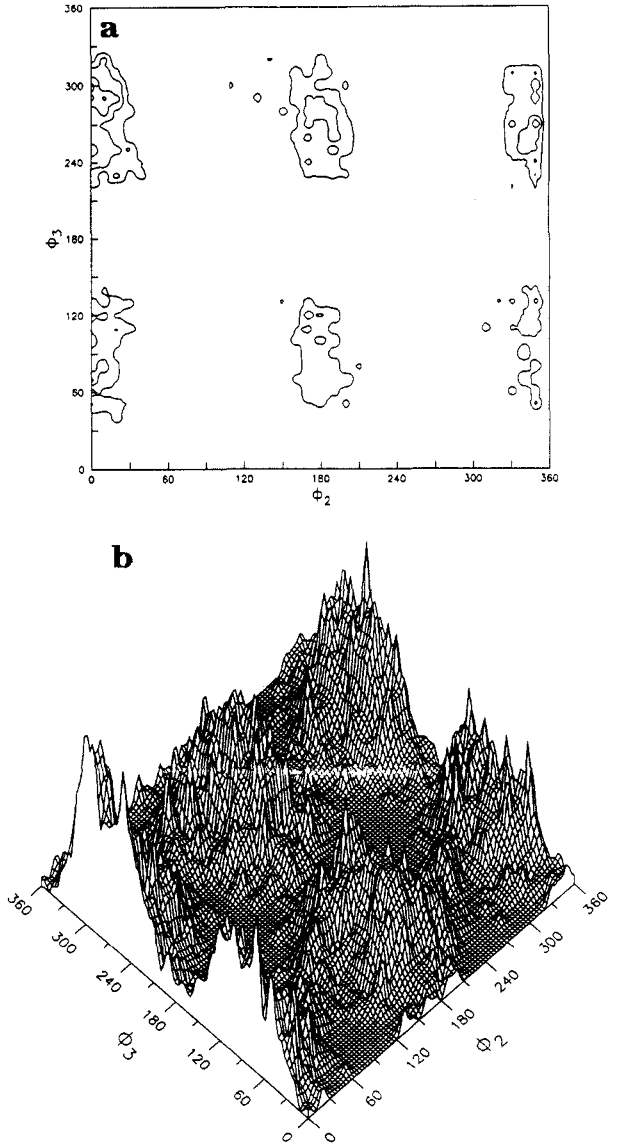

Figure 6. Distribution of probabilities, in 2D (a) and 3D (b) representations, for simultaneous rotations over ϕ_2 and ϕ_3 in the central ester residue of 4-chlorophenyl 4-(acetyloxy)-benzoate (CAB).

The molecule ACM can be obtained by replacing one H atom of the molecule APM by a Cl atom and therefore including a new contribution μ_3 to the total dipole moment of the molecule whose upper and lower limits would then be $\mu_{max} = \mu_1 + \mu_2 + \mu_3 \approx 6.3$ and $\mu_{min} \approx 0$. However, although the range of allowed values of μ are almost identical for molecules ACM and CAB, Figure 7 shows clearly that the behavior of both molecules is quite different. Thus, while the time evolution of the

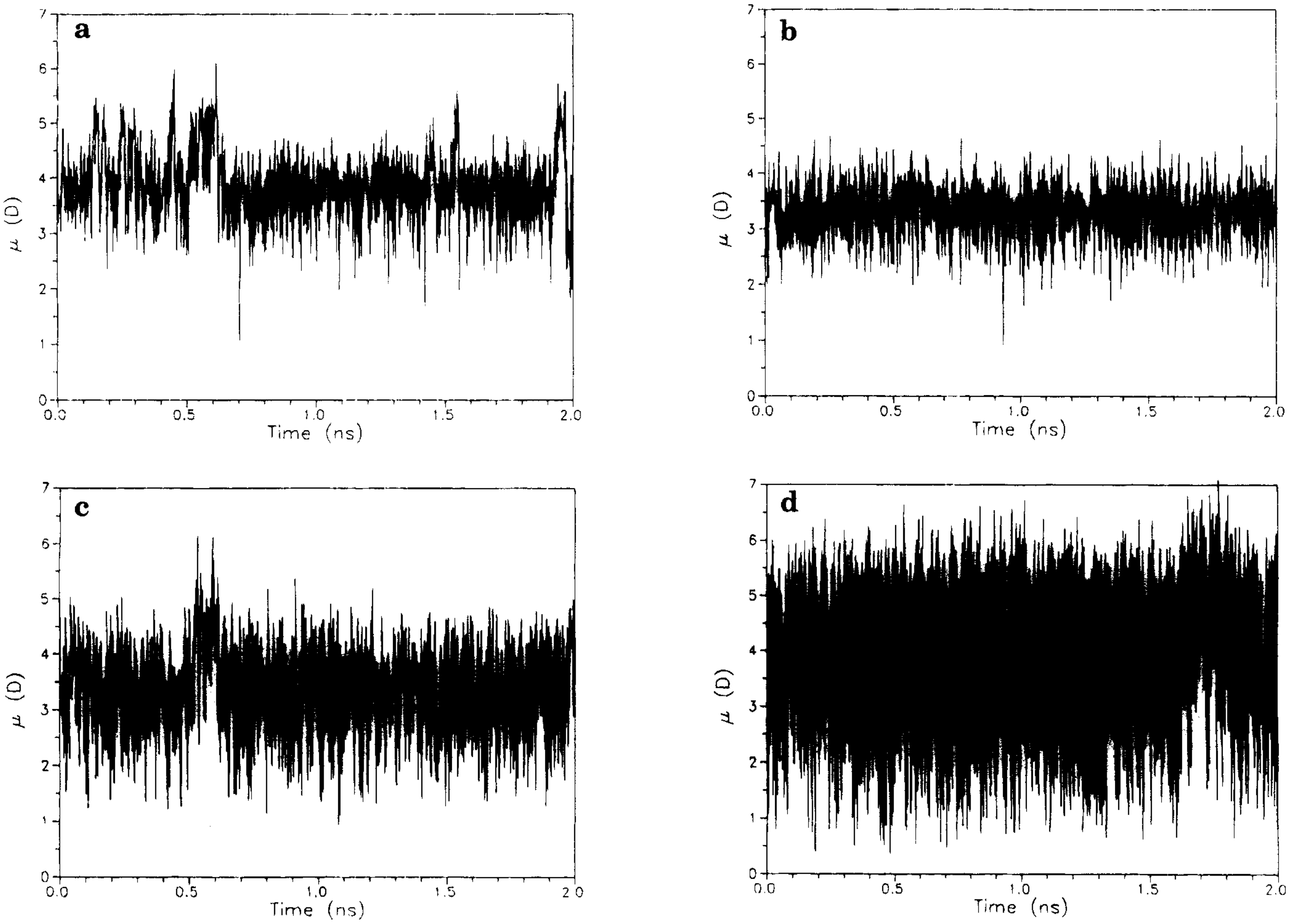

Figure 7. Evolution with time of the total dipole moment of 4-chlorophenyl 4-(acetyloxy)benzoate (CAB) (a), [4-(acetyloxy)phenyl](4-chlorophenyl)methanone (ACM) (b), [4-(acetyloxy)phenyl](phenyl)methanone (APM) (c), and bis[4-(acetyloxy)phenyl]methanone (BACM) (d).

Table 2. Experimental and Calculated Values of Dipole Moments for 4-Chlorophenyl 4-(Acetyloxy)benzoate (CAB), [4-(Acetyloxy)phenyl](4-chlorophenyl)methanone (ACM), Bis[4-(acetyloxy)phenyl]methanone, and [4-(Acetyloxy)phenyl]phenylmethanone (APM)

molecule	$\langle\mu^2\rangle$, D^2 (exptl)	nm^2, D^2 uncorr	$\langle\mu\rangle$, D (calc)	$\langle\mu^2\rangle$, D^2 (calc)
CAB	16.8	9.1	3.88	15.5
ACM	11.2	14.5	3.28	11.2
APM[a]	12.7	11.9	3.33	11.9
BACM	14.3	14.8	3.93	16.9

[a] Reference 11.

dipole moment of BACM covers practically the whole range of allowed values, most of the conformations adopted by ACM have values of dipole moment in the range 3.0 ± 0.5 D giving averaged values of $\langle\mu\rangle = 3.28$ D and $\langle\mu^2\rangle = 11.2$ D^2, this last average being noticeably smaller than the value $nm^2 = 14.5$ that would be obtained by adding uncorrelated contributions. The reason for the different behavior of ACM and BACM lies in the number of allowed relative orientations of the contributions $\mu_2 - \mu_1'$ in CAB or $\mu_2 - \mu_3$ in ACM. Thus, while in the case of BACM any pair of contributions is separated by at least two rotational angles, so that the three contributions are relatively independent, in ACM the relative orientation of μ_2 versus μ_3 is fixed;[22] both contributions are coplanar and make an angle of ca. 120° so that they behave as a single contribution having a modulus of $\mu_{23} \approx 2.6$ D and a direction close to the bisectrix of the angle defined by μ_2 and the C^*-C^{ar} bond (ϕ_2 rotational angle). If μ_1 and μ_{23} are taken as the contributions for the dipole moment of the whole molecule, the range of allowed values of μ is reduced to ca. 0.9–4.3 D and $nm^2 \approx 9.7$ D^2 would be obtained if these two contributions were uncorrelated. As Figure 7b and Table 2 show, the actual results for this molecule are slightly higher than those obtained with uncorrelated μ_1 and μ_{23} contributions.

The behavior of CAB is similar to that of molecule ACM. If the three contributions μ_1, μ_3, and μ_4 were uncorrelated, the allowed range for the dipole moment of molecule a would be ca. 0–5.2 D, while $nm^2 \approx 9.1$ would be obtained. However, the relative orientation of μ_3 and μ_4 is fixed[22] so that both components behave like a single dipole $\mu_{34} \approx 3.0$ D, with the only noteworthy difference with respect to ACM that μ_{34} is larger than any of the two contributions, while in the case of ACM, μ_{23} is smaller than μ_3. If the vectors μ_1 and μ_{34} were considered as contributions for the dipole moment of the molecule, the range of allowed values would be ca. 1.3–3.7 D and the uncorrelated value would be raised to ca. $nm^2 \approx 11.9$ D^2. As Figure 7a indicates, conformations having the total dipole moment in the upper part of the allowed interval are more frequently adopted than those having low polarity and consequently averaged values $\langle\mu\rangle = 3.88$ and $\langle\mu^2\rangle = 15.5$ noticeably larger than nm^2 are obtained for this molecule.

The temperature coefficient of the dipole moments of the model compounds is in all the cases relatively highly tough, at first sight, the value of this quantity should be close to zero. However, a close inspection of Figure 3 reveals interesting details that may explain this behavior. Actually, the figure shows an asymmetric distribution of lower energy conformational states with energy slightly increasing from 70 to 120 °C and from 290 to 240 °C. Increasing in temperature will favor the conformations of higher energy which in turn increase the dipole moment of the molecules and hence the positive temperature coefficient of the mean-square dipole moment of these compounds.

Finally, the near coplanarity of the Ph–CO–Ph moiety facilitates tridimensional molecular packing of the methanone derivatives, and, as a consequence, the thermograms of these compounds exhibit a well-developed single melting peak. The thermogram of 4-chlorophenyl 4-(acetyloxy)benzoate, however, presents in comparison a rather complicated pattern that seems to be strongly dependent on the thermal history.[23] This behavior presumably is a consequence of the fact that the rotational states about O–Ph bonds (90°, 270°) hinder the formation of crystals in which the two phenyl groups adopt the planar conformation in the crystal.

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(22) This is not completely true if the calculation is performed with partial charges and variations on bond lengths and bond angles are allowed; however, it is a good approximation for the purpose of a qualitative explanation.
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