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Comparative study on the dynamics, polarity, and thermal properties of the isomers of (4-acetyloxyphenyl)-(chlorophenyl)-methanone

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The effect of the location of the chlorine atoms on the dynamics, polarity, and thermal properties of the isomers derived from (4-acetyloxyphenyl)-(chlorophenyl)-methanone is discussed. The changes occurring in the dipole moments along the trajectories in their respective conformational spaces are rather large (between 6.0 and 0.3 D) for (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM), slightly lower for (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM), and relatively small (between 2 and 4 D) for (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone (4CPM). The values of the mean-square dipole moment of 2CPM, 3CPM and 4CPM, calculated from the evolution of their dipole moments along their respective trajectories, are 15.9, 13.1, and 11.2 D^2, respectively, in very good agreement with the experimental results 15.8, 13.4, and 11.2 D^2, respectively. Both melting and glass transition temperatures of the compounds are discussed in terms of their respective conformational entropies. © *1996 American Institute of Physics.* [S0021-9606(96)51442-X]

INTRODUCTION

The return to equilibrium of liquids perturbed by an external force field, as monitored by a physical property P sensitive to the perturbation, is customarily expressed by the simple exponential $P(t)-P_e=(P_o-P_e)\exp(-t/\tau)$, where τ and P_e are, respectively, the relaxation time associated with the relaxation process and the value of the property P at equilibrium. However, it is also well known that most of the relaxation processes are not described by a single relaxation time but rather by a distribution of relaxation times whose breadth increases as the complexity of the system increases. For some liquids, such as polymers, relaxation times may spread from picoseconds to seconds or larger, depending on temperature, concentration and molecular weight.[1,2]

When a liquid is cooled, a temperature is reached below which the ability of the liquid to flow is lost, becoming a glass. The temperature at which this occurs, called glass transition temperature, depends on the cooling rate. Glass–liquid transition is a general phenomenon exhibited by uncrystallizable systems, but even those with capability to develop crystallinity, when properly supercooled, also can become structurally a glass. In the glassy state there are noncrystalline packing modes for the atoms and molecules which, though of higher energy than those of the crystalline state, still have sufficiently low energy for the molecules can easily assemble. So long as the relaxation times are significantly shorter than the time scale of the experiment, the liquid moves in the configurational space among basins of similar depth. However, as the temperature of the liquid declines coming near the glass transition temperature, the mean-relaxation time anomalously increases and its temperature dependence is governed by the free volume; in other words, the relaxation time is related to the temperature by the Vogel–Tammann–Fulcher (VTF) equation.[3–5] A careful examination of the relaxation processes shows a single maximum frequency at $T \gg T_g$. However, as the temperature approaches T_g, the peak splits into a pair of maxima, the slow α peak, or glass–liquid relaxation, and the faster β peak, or secondary process. This behavior can be explained by assuming that interactions between atoms and molecules are comprised in a potential energy function $V(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)$ which depends on the spatial location $\mathbf{r}_i$ for each of these atoms, molecules, etc. As the temperature of the liquid decreases, the configuration point of the system, $\mathbf{R}(t)$, is forced into regions of increasingly rugged and heterogeneous topography in order to seek the ever deeper basins. As the temperature comes closer to T_g, the rarer and more widely separated these deep basins must be.[6,7] The α or glass–liquid relaxation entails long-range transitions between deep basins whereas the β relaxation is associated with elementary transitions between neighboring basins separated by low barrier energies.

The chemical structure governs the topology of the configurational space and, consequently, the dynamics of liquids. Among liquids made up by homologous flexible molecular chains, the larger is their conformational entropy, the lower is their glass transition temperature.[8,9] However, the height of barrier energies separating conformational states seems to be mainly responsible for the magnitude of T_g. In general, the presence of rigid residues in molecular chains will hinder conformational transitions about the skeletal bonds and the glass-transition temperature will be shifted to higher values. The same will occur with the location of the β relaxation process in the loss-temperature plane.

In order to get a deeper insight into the dynamics of liquids, it is important to obtain information on the effect of the chemical structure on the evolution with time of the physical properties of a series of homologous molecules. In this work, the time evolution of the dipole moment of the asymmetric chloro-isomers of (4-acetyloxyphenyl)-(chlorophenyl)-methanone, specifically, (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM) and (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM) is followed by molecular dynamics (MD), and further compared with that of the symmetric isomer, (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone (4CPM).[10] It is expected that the trajectories of the isomers in the conformational space will be strongly influenced by interactions between the ketone group and the chlorine atoms. The reliability of the MD calculations is checked by comparing the values of the mean-square dipole moment calculated from the conformational trajectories of the molecules with those experimentally determined. Attention is also paid to relate the molecular flexibility, as expressed by the conformational entropy, to the development of crystallinity in these compounds. This work forms part of a more general project carried out in our laboratories dealing with the study of the influence of the structure of the side groups on the relaxation processes of acrylic polymers.

EXPERIMENT

Materials

Aluminum chloride (Merck), boric acid (Riedel), 3-chlorobenzoic acid and 2-chlorobenzoic acid (Aldrich) were used as received. Thionyl chloride (Fluka), phenol (Merck) and acetic anhydride (Merck) were distilled prior to use. Carbon disulfide (Merck) was dried with MDI and distilled. All other analytical grade solvents and other chemicals from commercial sources were used as received.

Triphenyl borate(1)

A mixture of 300.0 g (3.18 mol) of phenol and 31.0 g (0.5 mol) of boric acid was slowly distilled at normal pressure until the temperature at the top of the fractionation column reached 180 °C. The excess of phenol was removed by vacuum distillation. The solid residue was column chromatographed using an activated aluminum oxide bead and CH_2Cl_2 as eluent. The eluent solution was evaporated and the residue of (1) was stored under vacuum to keep it dry. Yield 82.7 g (57%).

(4-hydroxyphenyl)-(3-chlorophenyl)-methanone (2) and (4-hydroxyphenyl)-(2-chlorophenyl)-methanone (3)

A general route was employed to produce both compounds, and that corresponding to (4-hydroxyphenyl)-(3-chlorophenyl)-methanone is as follows. A suspension of 25.0 g (0.16 mol) of 3-chlorobenzoic acid and 41.6 g (0.35 mol) of thionyl chloride in 50 mL of toluene was refluxed for 4 h. The resulting homogeneous solution was vacuum distilled to remove the solvent and the excess of thionyl chloride. The remaining oil was diluted with 25 mL of carbon disulfide and the resulting solution was added to a mixture of 13.5 g (0.047 mol) of triphenyl borate and 56.0 g (0.42 mol) of aluminum chloride in 25 mL of carbon disulfide. The reaction mixture was refluxed for 6 h, poured into an equal mixture of ice and 6N HCl and then heated until complete neutralization of the catalyst. A clear brown waxy residue was separated and dissolved in 300 mL of 1N NaOH to promote the displacement of the protecting borate group. The resulting solution was treated with activated charcoal, filtered and acidulated with concentrated HCl. The solid product was crystallized from methanol/water (60/40). Yield: 10.4 g (27.9%).

(4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM) (4) and (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM) (5)

Both compounds were produced by reacting their respective phenols (2) and (3) with acetic anhydride in an alkaline medium. The acetylated compounds were purified by passing through a chromatographic column using a basic aluminum oxide bead and dichloromethane as eluent; finally (4) was crystallized from toluene/hexane (1:1) whereas (5), which is liquid at room temperature, was distilled at high vacuum. The average yield was 80%.

^{13}C-NMR ($CDCl_3$) for (4): δ 21.5 (CH_3–); 127.8, 129.0, 129.4, 129.6, 130.1, 131.9 (C^{ar}–H); 134.1, 134.3, 139.5, 143.6 (C^{ar}–); 168.6 (–COO–); 194.7 (–CO–). ^{13}C-NMR ($CDCl_3$) for (5) δ 21.0 (CH_3–); 121.7, 126.6, 128.9, 129.9, 131.1, 131.5 (C^{ar}–H); 131.0, 133.8, 138.2, 154.7 (C^{ar}–); 168.5 (–COO–); 193.8 (–CO–).

Thermal characterization of the compounds

The synthesis of (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone used in the thermal experiments is described elsewhere.[10] Values of both the glass transition and melting temperature of the three isomers were obtained with a DSC4 Perkin–Elmer calorimeter at a heating rate of 10°/min. The thermogram corresponding to 2CPM exhibits a single endotherm in the neighborhood of −26 °C corresponding to the glass–liquid transition. The thermogram of 3CPM presents an ostensible peak corresponding to a melting process which seems to reflect some kind of polyformism in the crystal. However, the thermogram of quenched 3CPM from the melt exhibits a well developed glass–liquid transition, located in the vicinity of −47 °C, followed by an exothermic peak corresponding to the crystallization of liquid 3CPM and, finally, an endotherm arising from the melting process of crystalline 3CPM. This behavior is reflected in Fig. 1. The thermogram for 4CPM only presents an endotherm associated with the crystalline→liquid transition. Quenching of molten 4CPM does not produce a supercooled liquid, as occurs with 3CPM, but a crystalline solid.

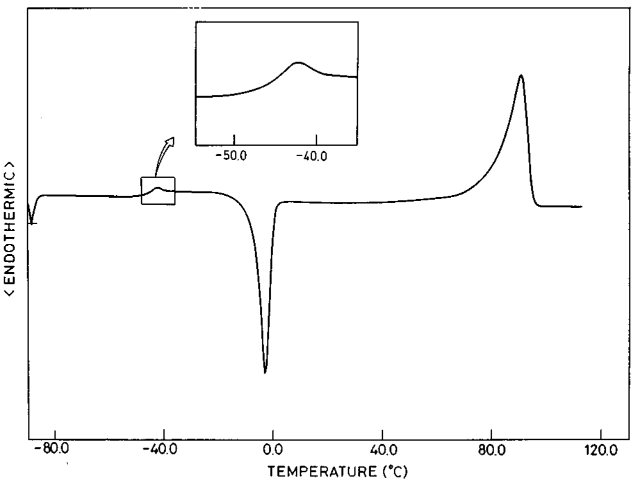

FIG. 1. Thermogram for quenched (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM), showing from low to high temperature the glass–liquid, crystallization and melting processes. The insert shows the glass–liquid transition in more detail.

Mean-square dipole moments

Experimental values of the mean square dipole moment $\langle\mu^2\rangle$ of 3CPM and 2CPM were obtained in benzene solutions using the procedure outlined by Guggenheim and Smith.[11,12] The method implies the determination of the total polarization of the solute which is proportional to the experimental value of $d\epsilon/dw$ in the limit $w\rightarrow 0$, where ϵ and w are, respectively, the dielectric permittivity of the solution and the weight fraction of solute. The polarization induced by the distortion of the electronic clouds by the electric field, which is proportional to dn/dw, where n is the index of refraction of the solution, was measured and subtracted from the total polarization. The atomic polarization was considered to be negligible. The values at 30 °C of $d\epsilon/dw$, dn/dw, and $\langle\mu^2\rangle$ for 3CPM and 2CPM are given in Table I. In this table the values of these quantities for (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone (4CPM), taken from Ref. 10, are also shown.

MOLECULAR DYNAMICS CALCULATIONS

The planar *all-trans* structures of both 2CPM and 3CPM are represented in Fig. 2. Rotational angles O–C^{ar}, C^{ar}–C, and C–C^{ar} are represented by ϕ_1, ϕ_2, and ϕ_3 respectively. Values of 180° were assigned to the *trans* states of these angles (i.e., as they are drawn in Fig. 2).

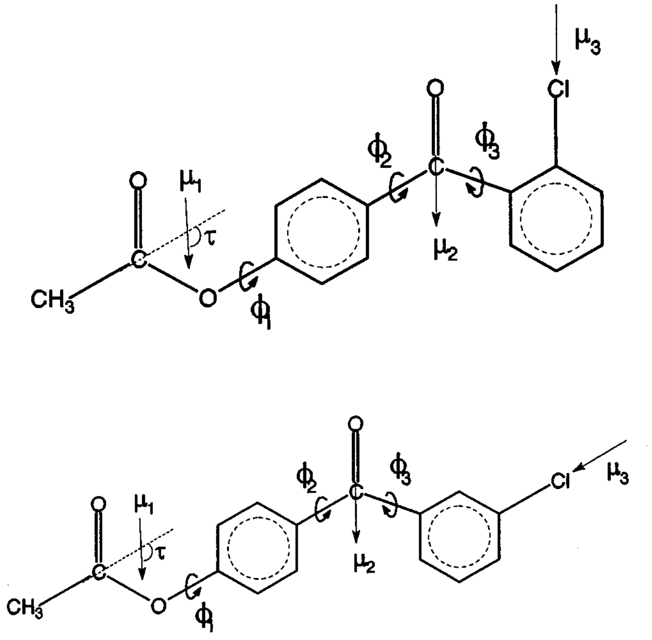

FIG. 2. Schematical representation of the planar *all-trans* conformation for (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM) and (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM) in which the value $\phi_i=180°$ was assigned to all the rotational angles. Arrows pointing from negative to positive centers of charges indicate the approximate direction of the contributions to the total dipole moment of each molecule.

TABLE I. Summary of dielectric results at 30 °C for (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM), (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM), (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone (4CPM).

Compound	$d\epsilon/dw$	$2n_1dn/dw$	$\langle\mu^2\rangle$,D^2
2CPM	6.33	0.25	15.8
3CPM	5.38	0.19	13.4
4CPM[a]	4.46	0.15	11.2

[a] Taken from Ref. 10.

Molecular dynamics (MD) simulations for the isolated molecules in the gaseous state were carried out with the SYBYL modeling package[13] employing the Tripos force field.[14] A value of $\epsilon=4$ was assigned to the dielectric permittivity for the evaluation of the Coulombic contributions to the potential energy. 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 starting point for the MD trajectories in which the Verlet algorithm[15] was employed to integrate the Newton equation of motion for each atom with a given value of time step δ, that was set to 1 fs (10^{-15} s) in all our calculations. The molecules were first warmed up from 0 K to the working temperature with increments of 20 K and allowing a relaxation interval of 500 time steps in each intermediate temperature. Once the working temperature was reached, the simulations were continued for 4 10^6 time steps (i.e., during 4 ns) at constant temperature and the data of interest were recorded every 500 fs.

Partial charges, computed with the MOPAC program and the AM1[16,17] procedure, were assigned to each atom of the molecules. The values thus obtained are shown in Fig. 3. These charges were used both to calculate Coulombic interactions and to evaluate the dipole moment of each one of the conformations analyzed along the MD trajectories.

The *a priori* probability distribution for the rotational angles ϕ_1, ϕ_2, and ϕ_3, taken as independent of their neigh-

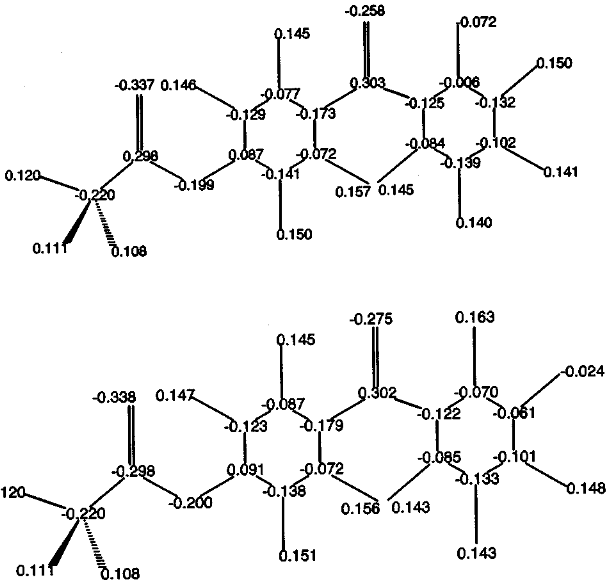

FIG. 3. Partial charges (in electronic units of charge) assigned to each atom of (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM) and (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM). These charges were used for all the calculations presented in this work. See the text for details.

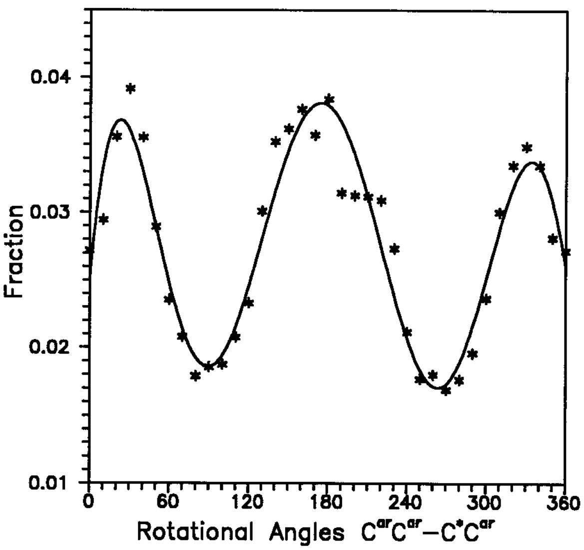

FIG. 5. Distribution of probabilities for the ϕ_2 and ϕ_3 rotational angles (i.e., rotations around $C^{ar}C^{ar}$–C^*C^{ar} bonds in the ketone group of (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM). The asterisks represent the actual results of MD simulations while the solid line is a least squares fitting drawn to show up the shape of the maxima.

bors, was computed by evaluating the fraction of conformations along the MD trajectories in which the value of one of these angles lies within an interval of 10° (for instance, the fraction indicated below for $\phi_1=40°$ was computed by counting the number of conformations in which $35°<\phi_1<45°$). The results at 300 K are summarized in Fig. 4 for ϕ_1, and Fig. 5 for ϕ_2 and ϕ_3. The rotational behavior of both 2CPM and 3CPM is practically identical and coincides also with the results reported for 4CPM in a previous work.[10] Thus the preferred orientations for the ester residue are those placing ester and phenyl groups roughly perpendicular to each other (i.e., $\phi_1=\pm 90°$). On the contrary, the ketone residue is preferently located in the same plane that the phenyl ring (i.e., $\phi_2,\phi_3=0°$, 180°).

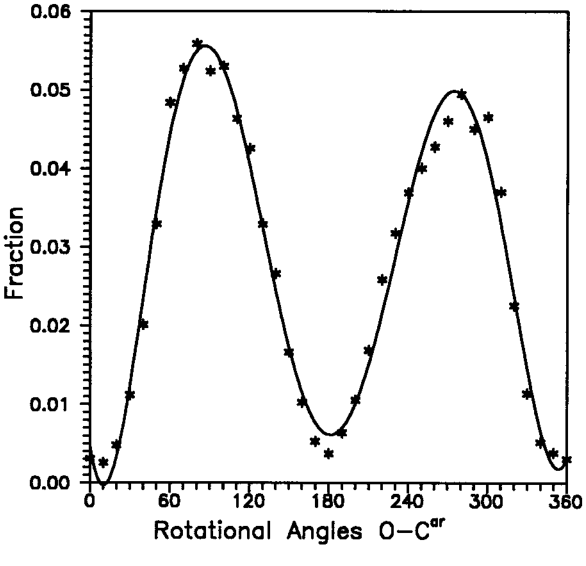

FIG. 4. Distribution of probabilities for ϕ_1 rotational angles (i.e., rotations around the O–C^{ar} bond of the ester residue). The curves are similar for the three isomers. The asterisks represent the actual results of MD simulations while the solid line is a least squares fitting drawn to show up the shape of the maxima.

The distribution of conditional probabilities for the simultaneous rotations of ϕ_2,ϕ_3 is also quite similar for the three isomers. Figure 6 shows, as an example, the 2D and 3D representations of this distribution for 3CPM at 300 K. The most important feature of this distribution is that the preferred states are not placed at the combinations of $\phi_2,\phi_3=0°$, 180° (which are the probability maxima for these angles when taken as independent), but displaced in ca. 30° from those states with displacements of the same sign in both angles. A more quantitative information about these probabilities is summarized in Table II where the sum of probabilities computed in the vicinities of each maxima is collected. The differences among these states are rather small and probably they are within the limit of accuracy of the calculations.

The evolution of the dipole moment with time at 300 K, represented in Fig. 7, shows a rather fast conformational interconversion from high to low polarity states. Values of mean-square dipole moments obtained along the MD trajectories are in excellent agreement with the experimental results.

DISCUSSION

Although the actual calculations of dipole moments along the MD trajectories were performed with partial

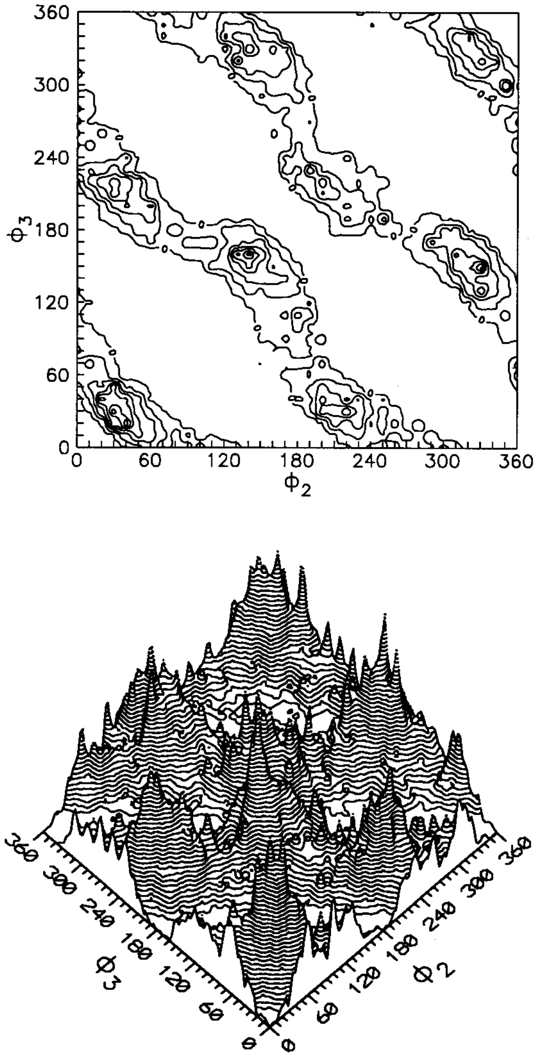

FIG. 6. Distribution of probabilities, in 2D and 3D representations, for the simultaneous rotations around the pair of bonds $C^{ar}C^{ar}$–C*–$C^{ar}C^{ar}$ in the ketone residue (ϕ_2 and ϕ_3 rotational angles) of (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM).

TABLE II. Conditional probabilities for the ϕ_2, ϕ_3 pair of rotations computed within ±40° intervals around the maxima of (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM) and (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM).

2CPM isomer

ϕ_2	ϕ_3 −30	ϕ_3 30	ϕ_3 150	ϕ_3 210
−30	0.105		0.088	
30		0.097		0.098
150	0.089		0.117	
210		0.127		0.077

3CPM isomer

ϕ_2	ϕ_3 −30	ϕ_3 30	ϕ_3 150	ϕ_3 210
−30	0.084		0.097	
30		0.099		0.098
150	0.096		0.101	
210		0.084		0.086

charges, it is possible to present an approximate and more intuitive analysis by adding group contributions to the dipole moment. The approximate directions of these contributions coming from ester, ketone and chlorophenyl groups, are represented by means of arrows (pointing from negative to positive centers of charges) in Fig. 2. Values of these contributions can be taken from experimental values of model compounds reported in the literature.[18] Thus a value of $\mu_1=1.7$ D (experimental result obtained for phenyl acetate) with a direction defined by an angle $\tau=123°$ between the dipole vector and the CH_3–C* bond[19] was used as contribution for the ester group; a dipole $\mu_2=3.0$ D (average of experimental results obtained for benzophenone) lying along the C═O bond was used for the ketone residue, and $\mu_3=1.6$ D (from chlorobenzene) in the direction of the C^{ar}–Cl bond was assigned to the chlorophenyl group. The results of this approximate analysis are summarized in Table III along with the experimental values and the results obtained with the actual MD calculations. If these three group contributions were exactly parallel, the molecule would have a maximum dipole moment of 6.3 D, while if they were antiparallel, the resulting dipole moment would be ca. 0.3 D. An inspection of Fig. 7 reveals that these are approximately[20] the limits between which the actual dipole moments of 2CPM and 3CPM oscillate. In fact the oscillations are slightly larger in 2CPM than in 3CPM because in the former case the relative orientation of μ_2 and μ_3 changes more with the ϕ_3 rotation than in the later isomer. Assuming that there was no correlation between the three contributions, a value of $\langle\mu^2\rangle=\Sigma\mu_i^2=14.5$ D^2 would be obtained for both molecules. This value lies between the experimental results for these two molecules, which indicates that positive correlations are slightly favored in the case of 2CPM, while the situation is just the opposite in the 3CPM isomer.

Addition of the three contributions for each one of the preferred conformations (i.e., the rotational isomers) summarized in Table IV gives the dipole moments collected in Table III. Mean square dipoles obtained with these values, assuming the same weight for all isomers, are summarized in the last row of Table III. Weighting the rotational isomers with the probabilities indicated in Table II produces rather small variations of these results. The values obtained with this latter procedure overestimate the experimental results, although the trend $\langle\mu^2\rangle$ (2CPM)>$\langle\mu^2\rangle$ (3CPM)>$\langle\mu^2\rangle$ (4CPM) coincides with that experimentally found. Consequently, calculations of these dipole moments with the standard rotational isomeric states (RIS) scheme would require to use smaller dipole contributions of each group than those indicated above.

The location of the chlorine atom in (4-acetyloxyphenyl)-(chlorophenyl)-methanone isomers, strongly affects the thermal properties of the corresponding isomer. Thus whereas 3CPM and 4CPM are crystalline compounds with melting points of 89 and 126 °C, respectively, 2CPM is liquid at room temperature with a glass transition temperature of −26 °C. On the other hand, 3CPM, unlike 4CPM, becomes a supercooled liquid when quenched from the melt, with a glass transition temperature of ca. −47 °C. Owing to the small variations in the polarity of the chloroisomers of (4-acetyloxyphenyl)-(chlorophenyl)-methanone, it is expected that intramolecular interactions rather than intermolecular ones may be held responsible for the differences observed in their thermal properties. Consequently, the fact that both 4CPM and 3CPM are crystalline at room temperature whereas 2CPM is liquid suggests that the conformational space of this latter compound must differ significantly from that of the crystalline compounds.

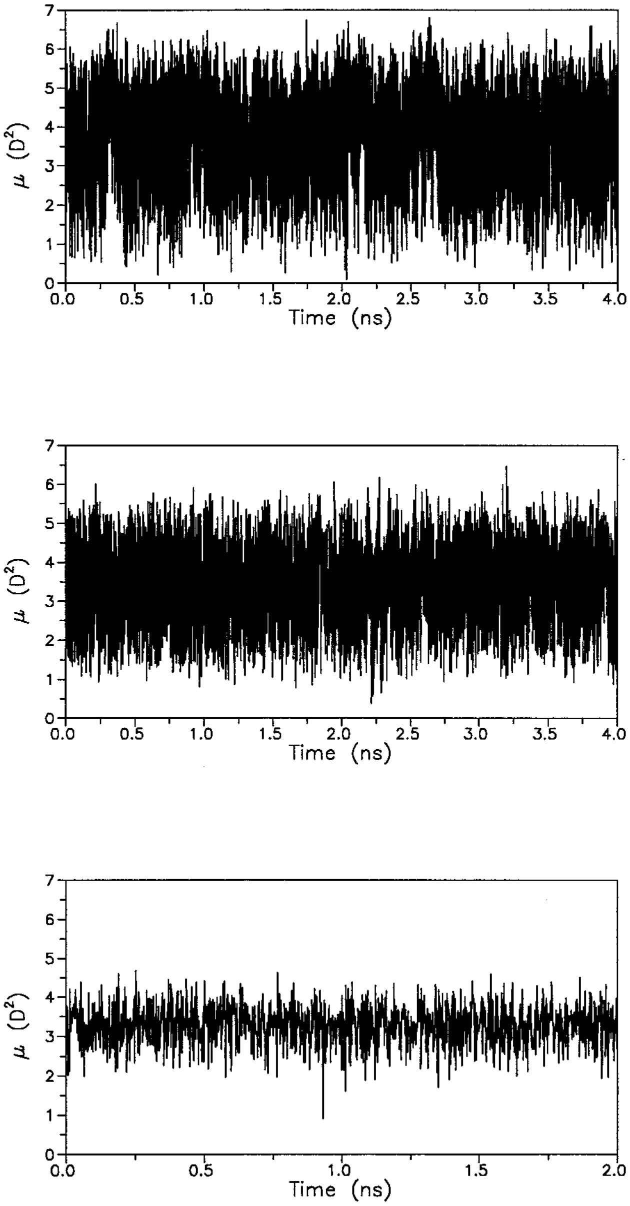

FIG. 7. Evolution with time of the total dipole moment of the isomers. From up to down: (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM), (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM) and (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone (4CPM).

TABLE III. Summary of experimental and calculated values at 300 K of dipole moments for (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM), (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM) and (4-acetyloxyphenyl)-(4-chlorophenyl)-methanone (4CPM).

Parameter	2CPM	3CPM	4CPM[a]
$\langle \mu^2 \rangle$ Experim.	15.7	13.4	11.2
$\langle \mu^2 \rangle$ MD calc.	15.9	13.1	11.2
$\langle \mu \rangle$ MD calc.	3.80	3.47	3.28
$\langle \mu^2 \rangle$ Uncorrel.	14.5	14.5	14.5
$\langle \mu^2 \rangle$ RIS	19.6	19.6	

[a] Taken from Ref. 10.

The distribution of the probabilities of the rotational angles about the bonds flanking the ketone group of 2CPM are shown at two temperatures in Figs. 8 and 9. Two maxima about C^{ar}–C* bonds are observed which correspond to the rotational angles (0°, 180°) at which the phenyl linked to the ester group is coplanar with the ketone group. As the temperature increases, the conformers population in the neighborhood of these two rotational angles slightly decreases. Calculations of the rotational population about the bond linking the ketone group to the 2-chlorophenyl group (C*–C^{ar}) show that the maxima are shifted from 0°, 180° to 60°, 200°. As the temperature increases the population of rotational states is nearly similar for the rotational angles lying in the range 60°–200°, in sharp contrast with what occurs for 3CPM and 4CPM where well defined potential wells about bonds flanking the ketone group occur. Consequently, strong intramolecular interactions between the chlorine atom and the ketone group hinder the coplanar conformation of the $-C_6H_4-CO-C_6H_4Cl$ moiety in 2CPM thus impeding the development of crystalline order in this compound.

Since the molecular isomers have similar polarity, it is expected that their glass transition temperature is governed by the molecular flexibility which is conveniently expressed in terms of either the rotational partition function, Z, or the conformational entropy, ΔS_c, this latter quantity being more convenient because it does not depend on the reference state. The conformational entropy is currently expressed by

$$\Delta S_c = -k_B \sum_i p_i \ln p_i,$$

where k_B is the Boltzmann constant and p_i is the probability of the conformation i which also can be written as

$$p_i = \frac{\exp(-E_i/k_B T)}{Z},$$

where E_i is the energy of the conformation i. The fact that the value of the glass transition temperature of 3CPM, −47 °C, is nearly 21 °C below that of 2CPM suggests a slightly higher freedom of rotation about the two consecutive C^{ar}–CO–C^{ar} bonds in the former compound. This fact, rather than differences in conformational entropies may be held responsible for the lower T_g of 2CPM. It should be stressed in this regard that the values conformational entropies associ-

TABLE IV. Dipole moments (D) calculated by adding group dipoles (see Fig. 2), for the preferred orientations of (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM) and (4-acetyloxyphenyl)-(3-chlorophenyl)-methanone (3CPM).

	2CPM (ϕ_1=90)				2CPM (ϕ_1=270)			
	ϕ_3				ϕ_3			
ϕ_2	−30	30	150	210	−30	30	150	210
−30	2.92		4.51		3.66		6.04	
30		3.59		5.98		3.02		4.48
150	3.65		6.04		2.89		4.43	
210		3.03		4.55		3.60		5.98
	3CPM (ϕ_1=90)				3CPM (ϕ_1=270)			
	ϕ_3				ϕ_3			
ϕ_2	−30	30	150	210	−30	30	150	210
−30	2.69		4.36		2.77		5.43	
30		2.76		5.42		2.72		4.31
150	2.79		5.45		2.66		4.28	
210		2.74		4.38		2.73		5.40

ated with the pair of bonds indicated above are nearly similar (13.2 and 13.0 cal mol^{-1} K^{-1} for 3CPM and 2CPM, respectively, at 30 °C).

The evaluation of the melting entropy, ΔS_m, requires to know with enough precision the melting enthalpy and melting temperature of the crystalline compounds. However, whereas the melting peak of 4CPM is sharp and nearly independent on the crystallization conditions, the melting endotherm of 3CPM shows a strong dependence on the undercooling. Thus the value of ΔH_m for 3CPM increases from 4.11 kcal mol^{-1}, obtained in the conditions indicated in Fig. 1, to 6.04 kcal mol^{-1} if the crystallization of liquid 3CPM is performed at 30 °C. The melting enthalpy for 4CPM is somewhat higher than that of 3CPM, its value being 1.65 kcal mol^{-1} higher than that of the latter compound. It should be pointed out that the values of both ΔH_m and T_m were obtained in conditions far from equilibrium and, consequently, the results can be considered only semiquantitative. The values of the melting entropy thus obtained are 16.5 and 19.2 cal mol^{-1} K^{-1}, respectively, for 3PMC and 4PMC. The melting behavior of these compounds may be critically interpreted in terms of the conformational entropy ΔS_c, which is related to the entropy of fusion ΔS_m, as indicated below. Actually, this parameter can be expressed by the following:

$$\Delta S_m=(\Delta S_m)_V+\int\left(\frac{\partial S}{\partial V}\right)_T dV=(\Delta S_m)_V+\int\left(\frac{\partial p}{\partial T}\right)_V dV,$$

where $(\Delta S_m)_V$ is the melting entropy at constant volume. Boyd and Starkweather[21] have considered that ΔS_m involves the conformational entropy ΔS_c and two additional terms,

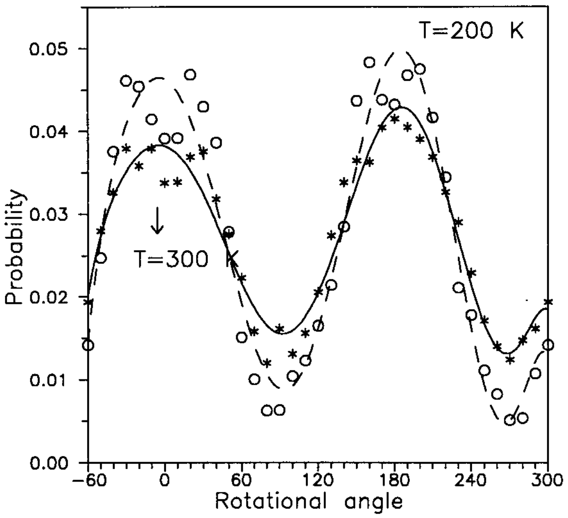

FIG. 8. Distribution of probabilities about OC^{ar}C^{ar}–C*(O*)C^{ar} bonds in (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM), at the temperatures indicated.

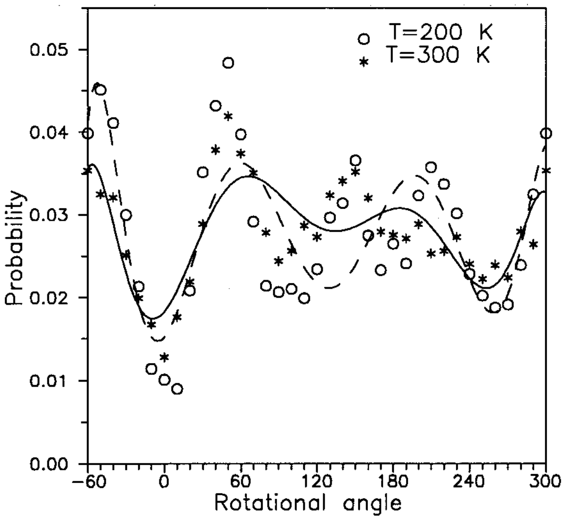

FIG. 9. Distribution of probabilities about C^{a}C*(O*)–C^{ar}C^{ar} bonds in (4-acetyloxyphenyl)-(2-chlorophenyl)-methanone (2CPM), at the temperatures indicated.

one of them negative, which corresponds to the packing of the molecules within the crystal, and the other positive, arising from long distance disorders. Based on metallographic results, these authors assign the value of 0.86 R to the negative contribution. According to this

$$(\Delta S_m)_V = \Delta S_c - 0.86R + \Delta S_d .$$

It has been argued that for some systems, such as polyethylene, the molecular packing and long distance disorder contributions to the melting entropy are similar leading to the assumption $\Delta S_c \cong (\Delta S_m)_V$. The calculated values of ΔS_c of crystalline 3CPM and 4CPM compounds at their respective melting temperatures, 17.1 and 17.3 $\mathrm{K}^{-1}\ \mathrm{cal\ mol}^{-1}\ \mathrm{K}^{-1}$, are close to the semiquantitative values of ΔS_m indicated above. The similarity of these values suggest that differences in packing the molecules in the crystal rather than differences in the molecular flexibility may be held responsible for the higher melting temperature of the 4CPM isomer.

ACKNOWLEDGMENT

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