Density Functional Study of Reactions of Phenoxides with Polycarbonate

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Density functional calculations with simulated annealing have been used to study the reactions of chains of bisphenol A polycarbonate (BPA-PC) with sodium phenoxide (NaOPh), diphenyl carbonate (DPC), and tetraphenylphosphonium phenoxide (PPh_4OPh). These calculations extend our work on the reactions of LiOPh, NaOPh, and phenol with the cyclic tetramer of BPA-PC. We study, in particular, chain growth catalyzed by NaOPh and PPh_4OH. The energy barriers for reactions with PPh_4OPh are somewhat larger than those involving LiOPh and NaOPh, but they are significantly lower than those involving phenol (HOPh), due in part to the collective rearrangement of phenyl groups in the reacting molecules. We discuss in the Appendix the bonds between alkali metal atoms (Na in the present calculations) and other atoms (here oxygen) that are analogous to the more familiar "hydrogen bonds".

I. Introduction

Phenoxides, particularly those of lithium (LiOPh) and sodium (NaOPh), are widely used as nucleophilic reactants, examples being the Kolbe−Schmitt reaction[1] (carboxylation of NaOPh to salicylic acid) and their use to initiate polymerization in cyclic carbonates.[2] In a recent paper,[3] we described density functional calculations of the reactions of phenol, LiOPh, and NaOPh with the cyclic tetramer of bisphenol A polycarbonate (BPA-PC). This polymer has important industrial applications and has served as a prototype for both theorists and experimentalists.[4] An ideal model for BPA-PC chains is provided by the cyclic tetramer. It has a strain-free structure with the same local bonding, it has been isolated and analyzed spectroscopically,[5,6] and the structure of its crystalline form has been determined by X-ray diffraction.[6] Its large, open structure shows no hindrance to ring-flipping or cis−trans−trans−trans isomerization about the carbonyl group.[6]

Our calculations showed that attack by LiOPh and NaOPh led to ring-opening polymerization,[2] giving rise to a "living" polymer.[7] There is no measurable exotherm for the reaction of LiOPh with the cyclic tetramer (enthalpy change less than 0.3 kcal/mol),[8] and the results were consistent with this picture. The high barrier found for the reaction of phenol with the cyclic tetramer is in accordance with the low reactivity measured in the phenol−PC system.

We extend these calculations here to other reactions involving BPA-PC; in particular, exchange reactions of phenol-terminated PC chains with NaOPh and tetraphenylphosphonium phenoxide, PPh_4OPh. The density functional (DF) method[9] we use is free of adjustable parameters and, when combined with molecular dynamics (MD),[10] allows us to avoid geometrical structures corresponding to unfavorable local minima in the energy surface. The method is described in our earlier applications to organic molecules,[3] and necessary details are provided in section II. Calculations of the isolated reactant molecules are described in section III, and the reactions with PC chain segments are described in section IV. We summarize our findings in section V. Na and Li atoms form bonds to other atoms that are similar to the familiar "hydrogen bond", and we discuss this in the Appendix.

II. Method of Calculation

The method of calculation was described in detail previously.[11,12] The electron−ion interaction is represented by ionic pseudopotentials with the (nonlocal) form suggested by Troullier and Martins.[13] We use periodic boundary conditions and an orthorhombic unit cell with lattice constants appropriate for the reaction under consideration.[14] We expand the orbitals in terms of a plane wave basis (kinetic energy cutoff of 35 au) using a single point ($k = 0$) in the Brillouin zone. Density functional calculations presently require an approximation to the exchange-correlation energy. Our previous calculations on organic molecular crystals[15] indicated that the approximation of Perdew, Burke, and Ernzerhof (PBE),[16] which is relatively simple and free of empirical input, is suitable in this context. It is used in the present work.

Computer simulations cannot sample all possible reaction paths. The most favorable found will depend on the initial geometry, the points chosen on the path, and the accuracy of the relaxation procedure, so that detailed comparisons of different reaction paths and energy barriers are not simple. The energy surfaces are studied in the present work by adopting a reaction coordinate R_C, e.g., the distance between the C atom of a carbonate group in the ring and the O atom on phenol or phenoxide, and varying R_C until a structural transformation or a large energy change takes place. For large values of R_C (typically >5 Å), the weak interaction between the reactants means that changes of 1 Å are possible. As the reaction proceeds, progressively shorter steps (0.5−0.2 Å) are necessary. For each value of R_C, we relax *all* other degrees of freedom of the structure using molecular dynamics,[17] until the energy gradients along the unconstrained directions are less than an appropriate value.[18]

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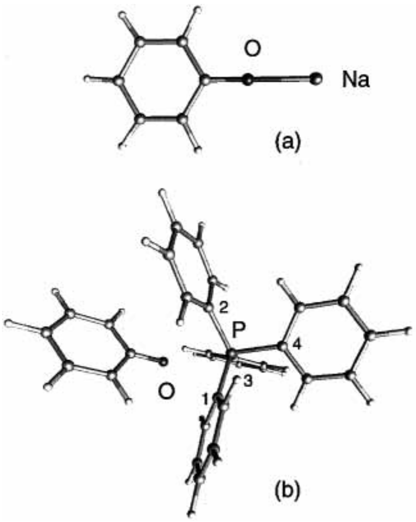


Figure 1. Molecules studied in the present work: (a) NaOPh; (b) PPh_4-OPh. The orientation of the dipole is along the horizontal axis in both cases. C atoms are gray; O atoms are black; H atoms are white; P and Na atoms are labeled.

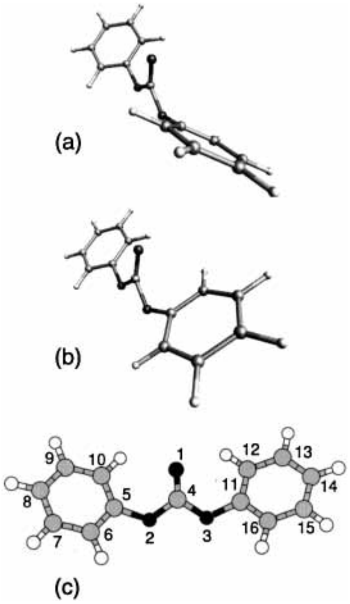


Figure 2. Diphenyl carbonate, DPC: (a) anti conformer, (b) syn conformer, (c) numeration scheme. C atoms are gray; O atoms are black; H atoms are white.

TABLE 1: Bond Lengths and Angles and Atomic Charges in PPh_4OPh[a]

atoms	distance (Å)	atoms	distance (Å)
P−C1	1.866	P−C2	1.855
P−C3	1.860	P−C4	1.903
P−O	2.577	O−C1	3.001
O−C2	2.811	O−C3	2.720

atoms	angle (deg)	atoms	angle (deg)
C1−P−C2	110.6	C1−P−C3	111.9
C1−P−C4	105.6	C2−P−C3	123.9
C2−P−C4	102.4	C3−P−C4	99.6
C4−P−O	170.5		
$C_{Ph}1-C1-P-C2$	133.0	$C_{Ph}2-C2-P-C3$	20.9
$C_{Ph}3-C3-P-C4$	52.8	$C_{Ph}4-C4-P-C1$	105.2

atom	charge[b] (e)	atom	charge[b] (e)
C1	0.32	C2	0.48
C3	0.48	C4	0.16
P	−0.33	O	−0.62

[a] The C atoms bonded to P are denoted C1, C2, C3, and C4 (see Figure 1b). [b] See ref 19.

III. Isolated Reactant Molecules

The reactions studied here are initiated by the following molecules: NaOPh (Figure 1a), tetraphenylphosphonium phenoxide (PPh_4OPh, Figure 1b), and diphenyl carbonate (DPC, Figure 2).

A. Sodium Phenoxide, NaOPh. The properties of isolated NaOPh have been discussed in ref 3, where we noted that its structure and properties differ from those of phenol. The dipole moment (12.0 D) and the charge on the terminal monovalent atom (0.91 e) are both much larger than the corresponding values in phenol (1.3 D and 0.35 e, respectively).[19] The O−Na bond is, of course, longer (2.11 Å) than the O−H bond in phenol (0.982 Å).[20]

The C−O−Na bond is linear ($\alpha_{COH} = 108°$ in phenol), but the low frequency of the bending mode (< 60 cm^{-1}) indicates a weak preference for the linear geometry.[21] Recent X-ray diffraction studies of crystalline NaOPh[1] show that the C−O bond length (1.33 Å) is the same as we find in the isolated molecule. The structural unit, however, is a four-membered ring, Na_2O_2, with each O atom bound to *two* Na atoms. It is not surprising that these Na−O bonds are substantially longer (2.33 Å) than the corresponding bond in the isolated molecule. The isolated phenoxyl radical has been discussed on numerous occasions, and we refer to ref 22 for a discussion of density functional and other calculations.

B. Tetraphenylphosphonium Phenoxide, $(PPh_4)OPh$. We have studied previously the reactions of the cyclic tetramer of BPA-PC with LiOPh, NaOPh, and phenol.[3] The range of cation size, electronegativity, and binding energies of these molecules can be extended by substituting suitable molecular cations for the terminal monovalent element. Here we have chosen tetraphenylphosphonium phenoxide, $(PPh_4)OPh$, where the phenoxyl group is capped by a tetraphenylphosphonium ion. An extensive study of molecular crystal structures by Dance and Scudder[23] showed that $(PPh_4)^+$ cations lead to intermolecular phenyl−phenyl conformations that are attractive, concerted, and widespread.

In Figure 1b we show the structure of $(PPh_4)OPh$, and representative bond lengths and angles are given in Table 1. The P atom and the neighboring four phenyl groups may be viewed as a deformed tetrahedron or a distorted trigonal pyramid around P, with P−C bonds in the base that are significantly shorter than that between P and the apex carbon. The phenoxyl ion is bound by ionic forces to the trigonal basis of the pyramid, and weak hydrogen bonds between its phenyl group (hydrogen donor) and one of the four others surrounding P (hydrogen acceptor) contribute to the stability of the molecule. (PPh_4)-OPh can therefore be regarded as an ion pair, $(PPh_4)^+OPh^-$.

The determination of the atomic charges, based on the analysis of the electrostatic field around the molecule,[19] shows that the positive charge binding the two ionic species is located on the three C atoms forming the base of the trigonal pyramid, while the P atom has a slight negative charge. Atomic charges are not uniquely defined,[24] and their numerical evaluation is often difficult. Nevertheless, the small negative charge on the P atom is a result that may be of wider relevance in the chemistry of $(PPh_4)OPh$. The calculated dipole moment (8.5 D) is smaller than in NaOPh (see above) and similar to the value in LiOPh (7.6 D).[3] The orientation of the dipoles in NaOPH and $(PPh_4)OPh$ is along the horizontal axis of Figure 1b.

TABLE 2: Bond Lengths and Angles and Vibrational Frequencies of Crystalline DPC Molecule[a]

atoms (Figure 2c)	calculated	experimental
	bond length (Å)	
O1−C4	1.213	1.174
O2−C4	1.355	1.338
O3−C4	1.359	1.348
O2−C5	1.407	1.415
C5−C6	1.392	1.382
C5−C10	1.392	1.380
O3−C11	1.410	1.413
C11−C12	1.392	1.376
C11−C16	1.390	1.383
	bond angle (deg)	
O1−C4−O2	127.5	123.7
O1−C4−O3	127.6	131.6
O2−C4−O3	104.9	104.6
C5−O2−C4	119.6	118.8
C11−O3−C4	118.6	118.3
C6−C5−O2	115.9	116.1
C10−C5−O2	121.5	121.2
C16−C11−O3	116.6	115.7
C12−C11−O3	120.9	121.2
C10−C5−O2−C4	59.2	58.9
C12−C11−O3−C4	61.6	53.8

mode	calculated vibrational frequency (cm^{-1})
C−H stretch	3150
C−C stretch	1590
C═O stretch	1778

[a] Calculated values are from the PBE functional; experimental values are from ref 29.

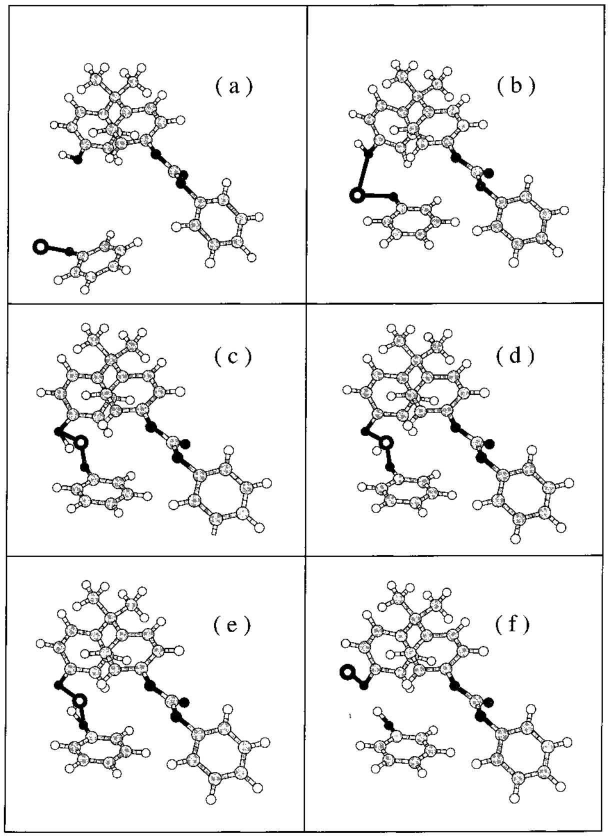


Figure 3. Snapshots of exchange reaction between NaOPh and phenol-terminated polycarbonate chain. C atoms are gray; O atoms are black; H atoms are white; Na atoms are denoted by bold circles.

The high-frequency part of the vibrational spectrum ($\omega \geq 1400$ cm^{-1}) is due to benzene ring modes and can be inferred from the results for the phenyl carbonate molecules.[25] The modes not present in polycarbonates include the aromatic C−O stretch at 1315 cm^{-1}. Modes with $680 \leq \omega \leq 716$ cm^{-1} have a large component from the stretching of the P−C bonds, and the weaker P−O bond has a stretching frequency of 527 cm^{-1}. Rigid oscillations of the benzene rings around P occur at lower frequencies: in-plane rotations of C_6H_5 occur for $320 \leq \omega \leq 440$ cm^{-1}, while libration and Ph−P−Ph bending modes have frequencies below 250 cm^{-1}. These relatively low frequencies indicate that reorientation of the aromatic rings coordinated to the P atom can occur, despite the inevitable steric hindrance.

C. Diphenyl Carbonate, DPC. Several conformers of the isolated diphenyl carbonate molecule have been studied previously using a force field optimized for polycarbonates[26] and Hartree−Fock and DF calculations.[27,28] In addition to a trans−trans form with both phenyl rings on the same side of the plane of the carbonate group (Figure 2b, syn conformer, C_s symmetry), there is an anti conformer (Figure 2a, C_2 symmetry) of slightly lower energy[27] and a cis−trans conformer.[28] All calculations predict the anti conformer (Figure 2b) to be the most stable by a small amount. The present DF calculations favor it over the syn form by only 1 kcal/mol.

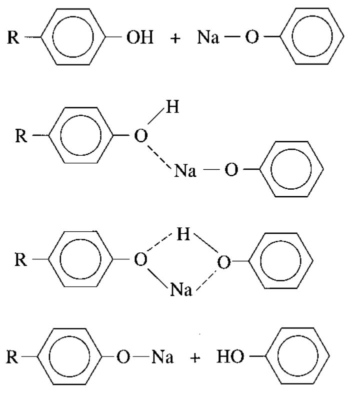
The diphenyl carbonate molecule crystallizes in the $P2_12_12_1$ orthorhombic structure. The structural unit is the syn conformer, i.e., not the form predicted to be the most stable in the gas phase, and there are four such units in a cell with lattice parameters $a = 6.062$ Å, $b = 7.242$ Å, and $c = 23.372$ Å.[29] Structural optimization starting from the experimental atomic positions yielded a geometry very close to the measured one (see Table 2).[30] The standard deviation of 0.12 Å for non-hydrogen atoms arises mainly from a slight rotation of the carbonate group with respect to the phenylene rings, the calculated dihedral angle of the two rings being 59.2° and 61.6°, compared with the measured values 58.9° and 53.8°. The only significant difference between the measured and calculated intramolecular bond lengths and angles occurs for the C═O distance, where the calculated value is ∼3% longer. The same effect was found previously in similar molecules,[15] indicating that the PBE approximation does not describe the details of the C═O double bond of the carbonate group as reliably as the rest of the molecule.

The computed intramolecular bond lengths and angles, and the atomic charges and vibrational frequencies are very similar for DPC (see Table 2) and the other carbonate molecules we discussed previously,[15,20] confirming that the covalent chemical bonds characterizing these molecules are transferable from one species to another. The PBE energy functional neglects dispersion interactions and leads to a low cohesive energy ($E_c = 4.8$ kcal/mol). This is consistent with our earlier calculations, although we know of no experimental estimates of the cohesive energy of DPC crystals.

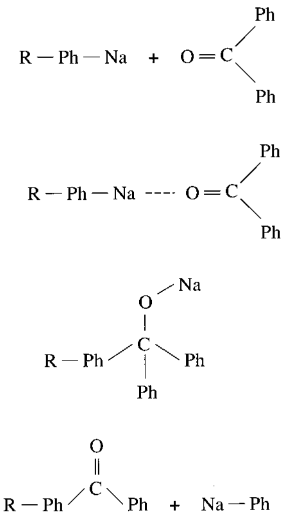
IV. Reactions of Polycarbonate with Phenoxides

We have described previously[3] the ring-opening polymerization of the cyclic tetramer of BPA-PC caused by the nucleophilic attack on the carbonate group by the metal termination of the phenoxyl group MOPh (M = Li, Na). However, PC chains sometimes terminate with phenol groups, as shown by the presence in infrared absorption measurements of the OH stretching mode ($\omega = 3600$ cm^{-1}). This has motivated the present study of reactions that exchange the M atom in MOPh with the H atom in phenol, since they could reactivate the polymerization process. The exchange reactions are then followed by the reaction of the product with a single diphenyl

SCHEME 1: First Stage of Reaction of Hydroxyl-Terminated PC Chain with Sodium Phenoxide



SCHEME 2: Second Stage of Reaction of Hydroxyl-Terminated PC Chain with Sodium Phenoxide[a]



[a] Ph denotes the phenyl group.

carbonate (DPC) molecule. The pair of reactions may be viewed together as chain growth catalyzed by MOPh, and we discuss the cases where M is the sodium and tetraphenyl phosphonium $(PPh_4)^+$ ions.

A. Sodium Phenoxide. *1. Reaction with OH-Terminated PC Chain.* The stages in this reaction, where the phenol terminated polycarbonate chain is represented by a short molecular analogue ("DPC-plus"), are shown in Figure 3 and Scheme 1. The small difference between the energies of the structures in Figure 3, panels a and f—in each case relative to the sum of the energies of the interacting molecules—is near the limit of our accuracy.[31] The following discussion refers to *total* energies, and the *free* energy balance would be altered in a condensed system or if solvent molecules were present.

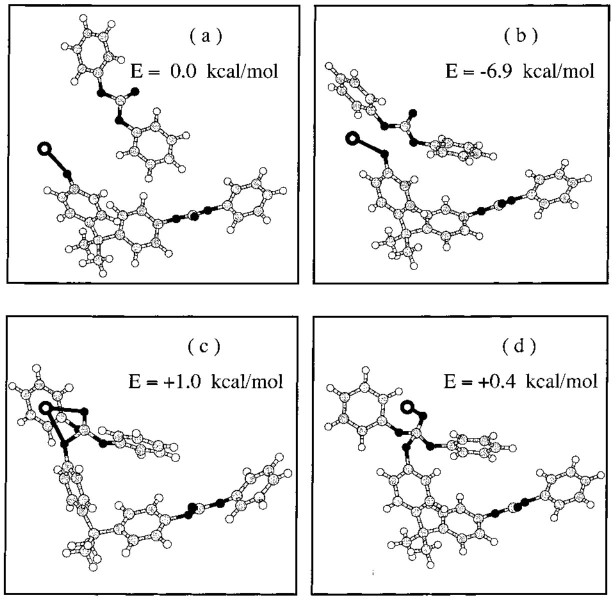


Figure 4. Snapshots of reaction between NaOPh-terminated polycarbonate chain and diphenyl carbonate (first stage). For symbols see Figure 3 caption.

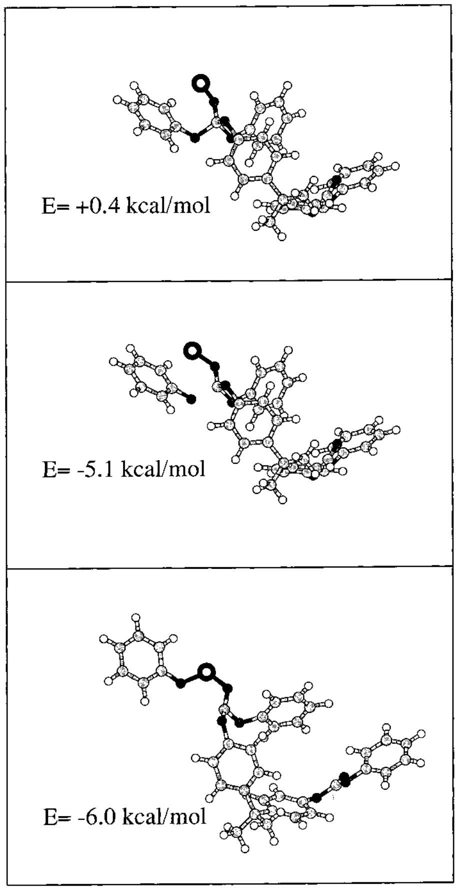


Figure 5. Snapshots of reaction between NaOPh-terminated polycarbonate chain and diphenyl carbonate (second stage). For symbols see Figure 3 caption.

The exchange reaction was started from configuration 3a, with the reaction coordinate being the distance between the O atoms adjacent to the H and Na atoms that are exchanged. The formation of an Na bridge between these two O atoms (Figure 3b) lowers the energy by 9.6 kcal/mol, and we show below (Appendix) that this is 2 kcal/mol stronger than an analogous H bond.[31] The Na bonds with the donor and acceptor O atoms are far from collinear (Figure 3b, $\alpha_{O-Na-O} = 61.0°$ at equilibrium). The bent OH phenol termination aids the formation of a structure with the two O atoms separated by only 2.5 Å, and there is a double donor−acceptor bond sharing the Na and H atoms (Figure 3c). The strength of the hydrogen bond leads to an unusually low O−H stretching frequency (2290 cm^{-1}), which lies between the C=O (1780 cm^{-1}) and the methyl C−H (between 2960 and 3060 cm^{-1}) stretching bands. The O−Na bond is also modified significantly, although the vibrational modes are delocalized, and the changes are more difficult to quantify.

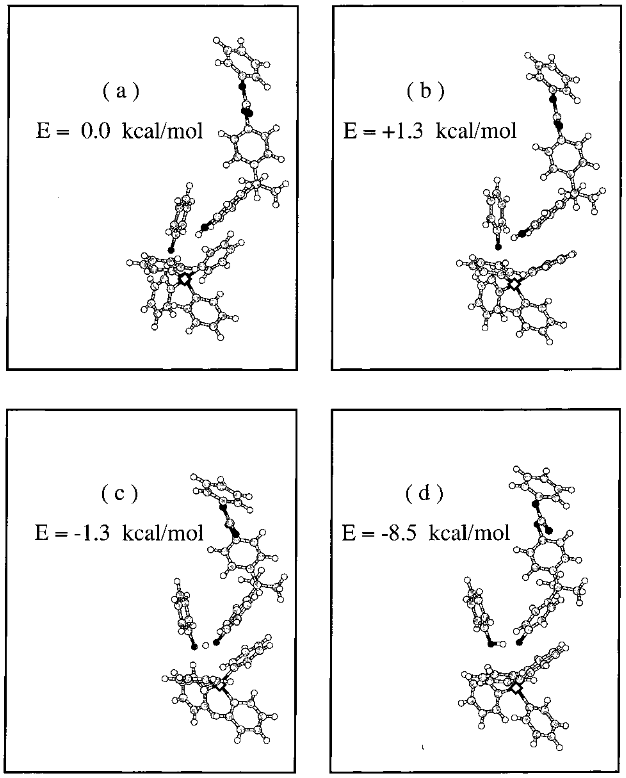


Figure 6. Snapshots of exchange reaction between PPh_4OPh and phenol-terminated polycarbonate chain. For symbols see Figure 3 caption.

The transformation from panel b to c of Figure 3 occurred spontaneously during the MD relaxation following a change in R_C. The effective potential for the H atom has a double well at this separation, and the low barrier between the minima has been determined by requiring a progressive increase in the distance between H and the original donor O. The barrier between panels c and d of Figure 3 is no more than −4 kcal/mol, so that the potential energy of the system during the exchange remains below the energy of the separated molecules. As in our previous calculations,[3] the transformation was completed by rotation of the O−Na bond around the C−O axis (Figure 3f). We have noted above that the energies of the structures in Figure 3, panels a and f, are almost identical.

2. Further Reaction with DPC. The reaction with DPC is shown in Scheme 2. The first stage of the reaction (Figure 4) shows an obvious similarity to the earlier work on reactions with the cyclic tetramer.[3] The coordination of the carbonate group changes from planar (sp^2) to approximately tetrahedral (sp^3) as the separation between O (phenol) and C (carbonate) is reduced, the energy variation is very similar (see Figure 4), and the Na atom in Figure 4d can rotate almost freely about the C−O bond. The "reaction" proceeds by rotation of the Na atom around this bond while a constant distance between the incoming molecule and the carbonate group is maintained.

The second stage of this reaction has been initiated from the uppermost configuration in Figure 5 and proceeds by analogy to the ring opening in the cyclic tetramer. The final configuration shows a very weak bond between a single phenol molecule and the Na atom, and the original "chain" has increased in length. Rotation of the Na atom in the opposite direction to that chosen here would break a different C−O bond, and the parallel to our earlier work is again evident.

B. Tetraphenylphosphonium Phenoxide, PPh_4OPh. *1. Reaction with PPh_4^+-Terminated PC Chain.* The hydrogen−cation exchange process discussed in the previous section for DPC-plus reacting with NaOPh has been repeated with the PPh_4-OPh molecule. The most obvious differences between the two cases are the size and ionicity of the cations involved and the degree of steric hindrance that must be overcome for the molecules to react. We have used the same procedure as above, reducing progressively the distance between the two (extremal) O atoms involved in the exchange.

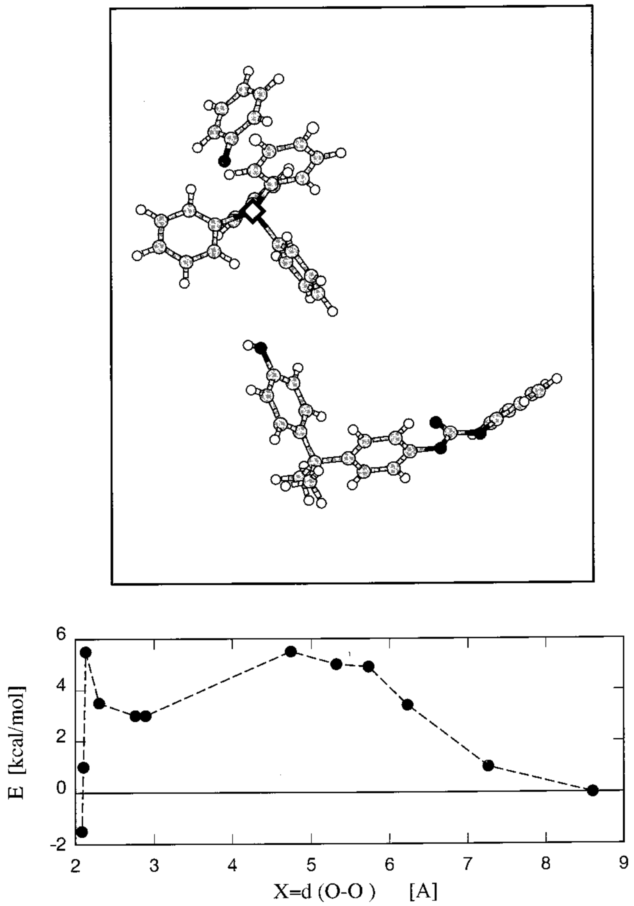


Figure 7. Starting configuration for "unfavorable" reaction between PPh_4OPh and phenol-terminated polycarbonate chain. The energies corresponding to different O−O separations are shown in the lower panel. The P atom is denoted by a bold square, and other symbols are given in the Figure 3 caption.

The results are summarized in Figure 6. The exchange occurs readily, although the relaxation following each change in the reaction coordinate is slow and computationally extremely demanding. The reactants have complicated structures, but the rings covalently bonded to P rotate in a *coordinated* (or collective) way as the two O atoms approach each other. This result is consistent with the low energy of the vibrational modes corresponding to rigid rotations of the phenyl groups.

The energy barriers involved in the reaction of PPh_4OPh are somewhat larger than those in the reaction of NaOPh, although much less than those encountered in reactions involving phenol. The surprisingly low barriers for PPh_4OPh are a consequence of coordinated rearrangements of the benzene rings. Such rearrangements imply a decrease in the system entropy, but the absence of a low-energy intermediate complex could facilitate the separation of the products and allow other reactions to occur.

It is difficult to isolate the effects of the relative orientation of the reactants in such complex systems, but their importance is evident if we consider a starting configuration with the exchanging O atoms on *opposite* sides of the P atom (Figure 7,

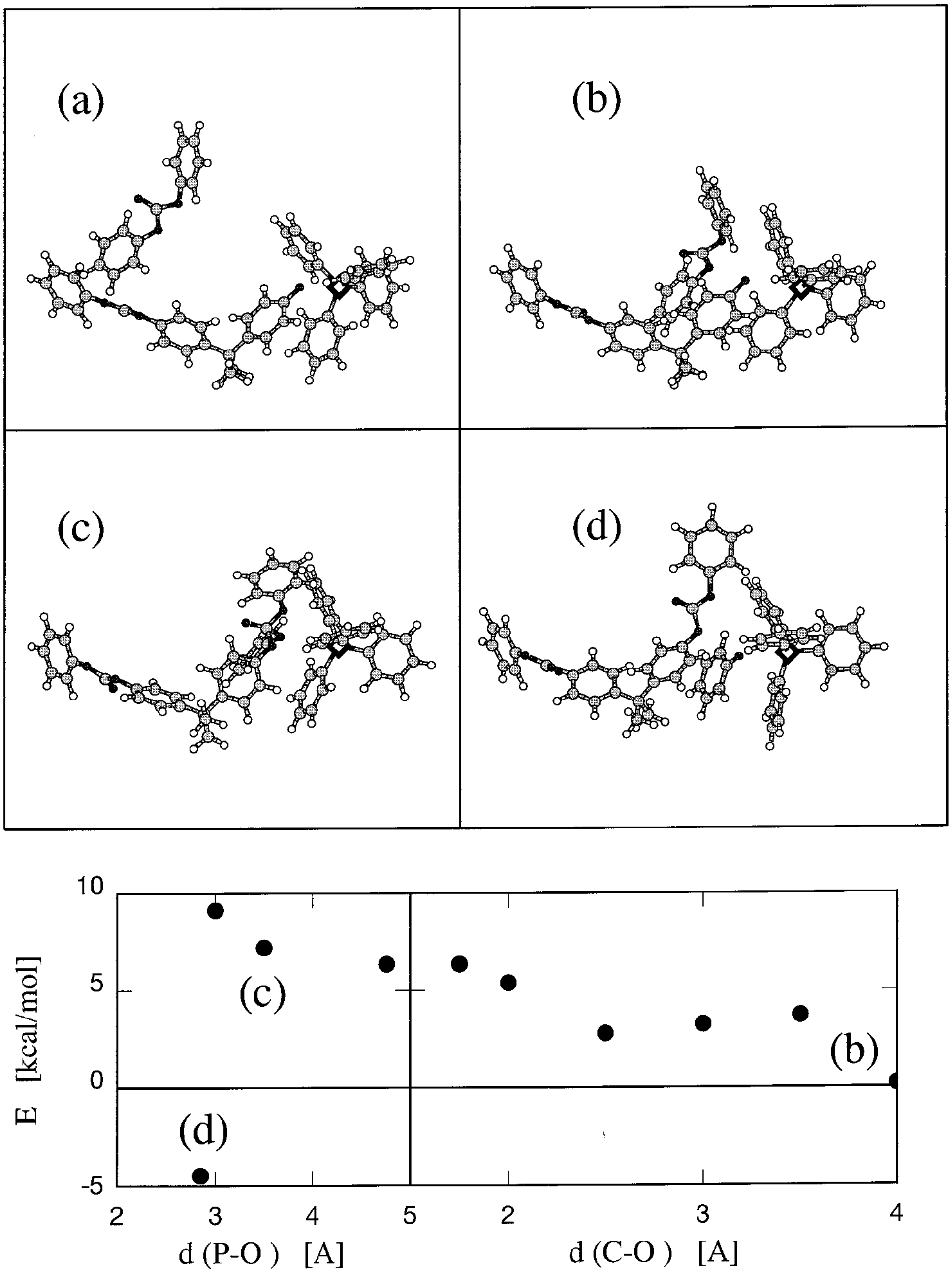


Figure 8. Snapshots of reaction between PPh_4OPh-terminated polycarbonate chain and diphenyl carbonate, with the corresponding changes in energy for the two reaction coordinates used (lower panel). The points on either side of the divide correspond to the same structure. For symbols see Figure 7 caption.

where we also show the energy variation). The relaxations are again exceedingly slow, but the reaction occurs without crossing a large energy barrier. We note that the constraint of *total energy* minimization has a cost in entropy. Estimates of the *free energy* barrier in systems of this complexity are outside the scope of DF calculations, but simulations involving classical force fields could provide useful information.

2. Further Reaction with DPC. The starting geometry for the reaction with DPC was derived from Figure 6d by removing the phenol molecule and allowing the system to relax to its energy minimum. The initial reaction coordinate was taken to be the distance between the C atom of the carbonate group of DPC and the O atom at the end of the chain, and the course of the reaction and the energy variation are shown in Figure 8. After formation of the tetrahedral CO_4 entity (Figure 8c), we used as reaction coordinate the distance between P and the O atom closest to it. This is shown in the left part of the energy plot. At the end of the reaction all constraints were removed, resulting in the PPh_4OPh molecule and a longer polycarbonate chain (Figure 8d). The weak interaction remaining between PPh_4OPh and the chain is reflected in the P−O bond, which is longer (2.84 Å) than in the isolated molecule (2.58 Å).

The course of this reaction shows interesting features: (a) First, the energy barrier (~9 kcal/mol) is larger than in the analogous reaction with Na but much less than the barriers we encountered in the reactions of phenol with the cyclic tetramer of BPA-PC. (b) A detailed study of the structural changes underlines the importance of the relaxation of the phenyl groups. In particular, the nonmonotonic variation in the total energy with changing reaction coordinate reflects in part the changes in the orientation of the groups in the reactants. Examples are the relatively stable structures formed when phenyl groups of the DPC and PPh_4 are aligned parallel or at right angles to each other.

V. Discussion and Concluding Remarks

We have performed density functional (DF) calculations on the reactions of chains of bisphenol A polycarbonate (BPA-PC) with sodium phenoxide, diphenyl carbonate (DPC), and tetraphenylphosphonium phenoxide. We have focused on nucleophilic attack on the carbonate group[32] and on reactions involving hydroxyl-terminated chains; in particular, chain growth catalyzed by NaOPh and $(PPh_4)OH$. The reactions are followed by fixing the value of an appropriate reaction coordinate and optimizing the positions of *all* other atoms. The total energy of the system and the forces and charges on all atoms are monitored throughout.

The results provide further evidence that DF calculations with simulated annealing can be performed for complex reactions involving over 100 atoms. The energetics are generally consistent with available experimental data, and vibration frequencies can be calculated for both the reactant molecules and stable intermediates. We should like to emphasize the following:

(1) There are recurring patterns of structural change: (a) The first major change is the formation of a bridge between the incoming molecule and the carbonate group, which lowers the energy by up to 15 kcal/mol. (b) The coordination of the carbonate group changes from planar (sp^2) to tetrahedral (sp^3). Formation of the tetrahedral unit leads to high mobility of neighboring ions (such as Na), leading in turn to the interchange of the role of the C−O bonds and further structural rearrangement.

(2) For NaOPh and PPh_4OPh, the reactions take place with low energy barriers, even if the direction of approach appears initially to be quite unfavorable. This is due in part to the collective rearrangement of groups, particularly phenyl groups, in the different reactants. The attractive interactions between phenyl groups are well understood, particularly the offset face-to-face (off) and edge-to-face (ef) conformations.[23] Such conformations occur often during the course of the reactions, and they are consistent with the nonmonotonic changes in the total energy as the reaction coordinates are changed. We have also observed structural changes that reflect the different orientations of the phenyl groups in the two isomers of DPC (Figure 2). The energies of the reactants and products in these reactions are generally similar, so that the course taken will also depend on entropy considerations. These are presently beyond the scope of the present DF method, and we are studying them using classical simulations.

(3) Despite the presence of phenyl groups that are both flexible and reactive, the PPh_4 structure shows similarities with a large alkali metal ion in the same situation. We note again that terminal alkali metal ions give rise to bonds that are analogous to the more familiar hydrogen bonds, and we discuss their nature further in the Appendix.

The extreme numerical demands of the present approach make it difficult to use routinely for studying complex reactions. Although entropy effects are not included, energy surfaces are an essential ingredient of *any* study of reaction paths, and the recurring patterns of structural change and the remarkable transferability of the energies involved provide insight into related reactions. An example would be the reaction of the $(PPh_4)OPh$ molecule with the carbonate group of a PC chain. The local atomic arrangement is the same as studied in section IV B 2, and the reaction should proceed analogously. The energy surfaces obtained here can also be used as a database for developing schemes, such as classical force fields, which are computationally much less demanding. Work in this direction is continuing.

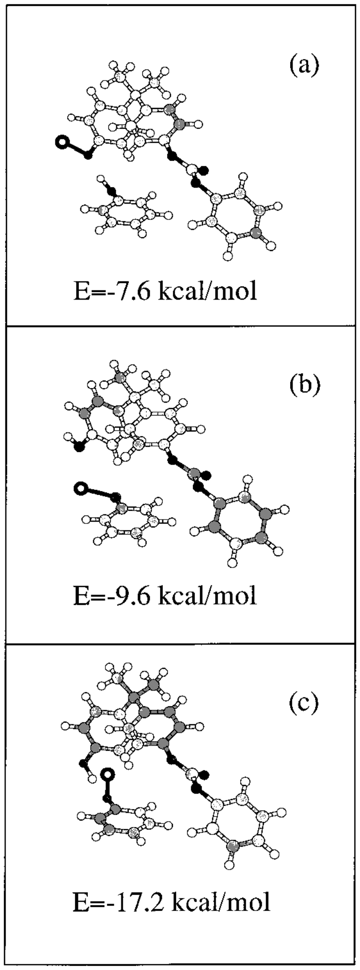


Figure 9. Hydrogen bond and alkali-metal (Na) bonds: (a) Phenol and NaDPC-plus; (b, c) NaOPh and DPC-plus. For symbols see Figure 3 caption.

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Appendix: Alkali metal analogy to "hydrogen bonds"

A hydrogen atom (H) covalently bound to atom A can form a bond to a second atom B whose electronegativity is higher than that of hydrogen. The latter, referred to as "hydrogen bonds" and denoted A−H•••B, are often weaker than covalent bonds, but they are very important. Alkali metal atoms have much lower electronegativities than H, so that analogues of these bonds could occur with more elements than hydrogen bonds themselves. We have found several examples during our studies of the phenoxides of Li and Na.

The reactions discussed in section IV A allow us to estimate the strengths of different intermolecular bonds, since the total energies of (a) NaOPh and "DPC-plus" and (b) phenol and

"NaDPC-plus" are almost identical and provide a suitable reference energy. All bonds in Figure 9 involve a donor−acceptor pair of O atoms, sharing either H (Figure 9a), Na (Figure 9b), or both H and Na (Figure 9c). The binding energies, relative to the energies of the isolated molecules (phenol and NaDPC-plus in Figure 9a, NaOPh and DPC-plus in Figure 9b,c), are also shown. The O−O separation is larger (3.80 Å) in the case of Na than in H (2.65 Å), but the bond is weaker in the latter. The additivity of the H and Na bonds in Figure 9c is probably accidental, but it demonstrates that significant intermolecular bonding can result from the combination of these relatively weak bonds.

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