Formation, Structure and Conformational Dynamics of Highly Substituted Diphenylcarbonates

Adelheid Godt,* Ömer Ünsal, and Volker Enkelmann[a]

Abstract: The symmetrical carbonates **5**–**8** were prepared from ethyl 4-hydroxybenzoates with aryl-, 4-(arylethynyl)phenyl-, arylethynyl- or arylbutadiynyl-substituents in the 3- and 5-positions, by reaction with triphosgene. The choice of base (pyridine, DMAP, NaH) had a strong influence on the conversion: For the synthesis of the carbonates **5** and **6**, it was sufficient to use pyridine as the base. However, for the synthesis of the carbonates **7** and **8**, NaH had to be used instead. Single-crystal X-ray structure analysis of these carbonates revealed that the substituents point towards the corners of a distorted tetrahedron with the carbonate group sitting in the middle of the tetrahedron and the two angular phenolic building blocks intersecting with an angle of 51–71°. In solution at room temperature, all four substituents are magnetically equivalent as a consequence of conformational flexibility. The two enantiomeric conformers of carbonate **5a** interconvert rapidly, probably via a perfect *trans* conformation with the plane of the Ar_{α} perpendicular to the carbonate plane. In the case of carbonates **6**–**8** this process is inhibited by unfavourable interaction of the long substituents at the benzoate moiety. The dynamic process, which has an energy barrier of 8–10 kcal mol^{-1}, is described in a simplified manner as a continuous rotation of the angular building blocks around the carbonate unit with the C_{aryl}–O bonds as the axes of rotation.

Keywords: carbonates · conformation dynamics · conformation analysis · template synthesis

Introduction

Recently we reported on diphenyl carbonate as a covalent template in the synthesis of a [2]catenane.[1] The formation of a mixture of entwined and non-entwined rings questioned the proposed geometrical organisation of the ring precursors by the carbonate linkage. Therefore, it was of pivotal importance to know the conformation of a carbonate derived from 3,5-disubstituted ethyl 4-hydroxybenzoates. X-ray structure analysis revealed the structure of such carbonates in the solid state. The higher molecular symmetry that was derived from NMR spectra of the carbonates in solution at room temperature raised the question about the conformational dynamics at the carbonate group. This was studied by NMR spectroscopy at different temperatures and provided insight into the influence of substituents on the carbonates' dynamics, particularly the energy barriers and the type of conformational interconversion. The conformational dynamics in carbonates is of significant interest for the correlation of the properties with the molecular structure and dynamics of polycarbonates.[2–8]

Results and Discussion

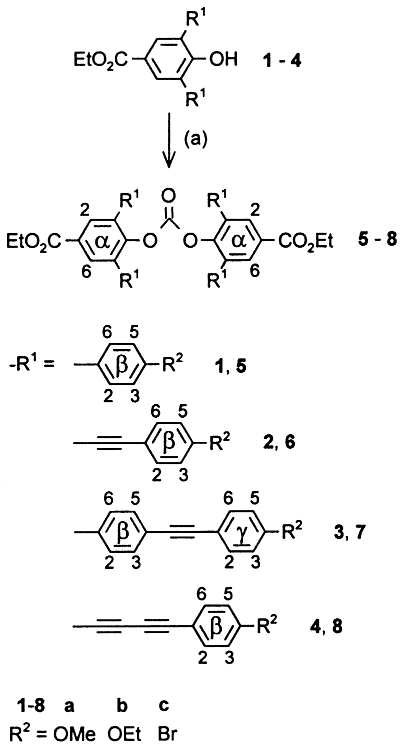
Synthesis: Diarylcarbonates are well-known compounds and synthetic difficulties were not expected.[9] Indeed, carbonates **5** and **6**[10] could be prepared from the corresponding phenols **1** or **2** and triphosgene[11] with pyridine (1.5–3 mol equiv) as the base (Scheme 1). The extent of the conversion was determined by ^{1}H NMR spectroscopy to be 85–91%. Surprisingly, the transformation of the phenols **3** and **4** into the carbonates **7** or **8**, respectively (Scheme 1), with triphosgene and pyridine (2–4 mol equiv) failed. The yields ranged from 0–25%. Heating to 60°C overnight did not increase the conversion of **4c**. When 4-dimethylaminopyridine (DMAP; 1.01–1.05 mol equiv) was used instead of pyridine, the degree of conversion of the phenols **3b**, **4b** and **4c** into the carbonates **7b**, **8b** and **8c** was 10, 59 and 21%, respectively. High conversion (82–99%) was finally achieved by preparation of the sodium phenolates from phenols **3b**,**c** or **4b**,**c** with sodium hydride in THF prior to the addition of triphosgene.[12]

The low conversion of the phenols **4** in the presence of pyridine or DMAP is most probably correlated with the instability of the corresponding carbonates **8** in the presence of pyridine or DMAP. When the carbonate **8b** or **8c** (≤ 0.01 M) was stirred in pyridine at room temperature for 24/48 h followed by aqueous work-up, mixtures of carbonate and the corresponding phenol were obtained. ^{1}H NMR spectroscopy

---

[a] Dr. A. Godt, Dr. Ö. Ünsal, Dr. V. Enkelmann
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, 55128 Mainz (Germany)
Fax: (+49) 6131-379100
E-mail: godt@mpip-mainz.mpg.de

0947-6539/00/0619-3522 $ 17.50+.50/0



Scheme 1. Synthesis of carbonates **5**–**8**. a) With **1** or **2**: triphosgene, pyridine, THF, room temperature; with **3** or **4**: i) NaH, THF, ii) triphosgene, room temperature.

revealed the cleavage of 38/73 % of **8b** and the cleavage of 78/100 % of **8c**. With DMAP (6 mol equiv) in THF at room temperature, carbonate **8b** was quantitatively converted into phenol **4b** within 6 h. Also, **6c** ($\leq$0.01 M) proved unstable in pyridine: after 24/48 h at room temperature 16/32 % of the carbonate had been cleaved. The successful formation of carbonate **6** from **2** (91 % conversion) and triphosgene in the presence of pyridine (3 mol equiv) is only an apparent contradiction. Evidently, in the equilibrium carbonate + pyridine $\rightleftharpoons$ phenolate + phenyloxycarbonylpyridinium, the carbonate side is favoured in the case of carbonates **6**, while it is disfavored in the case of carbonates **8**. The lability of the carbonates **6** and **8** in pyridine may be ascribed to the vinylogous anhydride structure.[13] The parent compound bis[4-(ethyloxycarbonyl)phenyl]carbonate, however, was much more stable: after 24/48 h in pyridine at room temperature, 7/25 % of ethyl 4-hydroxybenzoate had been formed. Moreover, contrary to carbonates **6c** and **8b**,**c**, the carbonates **5a** or **7b** did not react with pyridine (24 h, room temperature, $\leq$0.01 M solution) and only about 7 % of carbonate **7b** was cleaved by DMAP (51 mol equiv) over a period of 20 h in THF at room temperature. Therefore, the failure of the preparation of carbonates **7**, as described above, cannot be attributed to their lability in pyridine or DMAP.

Molecular structure of substituted diphenylcarbonates in the crystal: X-ray structure analysis of single crystals revealed very similar structures for the carbonates **5a**, **6c**, **7c** and **8c**.[14] Selected structural data are summarized in Table 1. For comparison, data of diphenylcarbonate (**9**)[15] and of the diphenylcarbonate of bisphenol-A (**10**)[16] are included in Table 1. As an example, the structure of **7c** in the crystal is shown in Figure 1.

The carbonate groups O-CO-O are planar. All carbonates show a *trans,trans* or W-shaped conformation[17] of the C_{aryl}-O-CO-O-C_{aryl} unit with deviations from an ideally planar W

Table 1. Selected angles and torsion angles of carbonates **5a**, **6c**, **7c**, and **8c**.[14] For comparison, corresponding data of diphenylcarbonate (**9**)[15] and of the diphenylcarbonate of bisphenol-A (**10**)[16] are shown.[a]

	5a	**6c** · $CHCl_3$	**7c** (**7c** · CH_2Cl_2)	**8c** · CH_2Cl_2	**9**	**10**[b]
ArO – $C_{carbonyl}$-OAr	105.2	103.4	105.6 (105.2)	105.2	104.6	106.5/105.5
C_{aryl}-O-$C_{carbonyl}$	116.2; 115.2	113.1; 116.1	117.3; 115.8 (116.0; 118.4)	119.5; 118.8	118.3; 118.8	119.3; 115.4/ 116.8; 117.2
C_{aryl}-C_{aryl}-O	116.4, 119.2; 119.4, 116.3	121.7, 118.9; 117.4, 119.0	117.7, 118.9; 119.0, 117.5 (117.3, 117.9; 117.0, 120.9)	117.6, 121.2; 120.1, 117.0	115.7, 121.2; 121.3, 116.1	122.9, 115.6; 118.9, 119.6/ 117.9, 120.0; 118.3, 120.0
α(C_{aryl}-O-$C_{carbonyl}$-$O_{carbonyl}$)	– 4.2; – 3.5	8.8; 2.6	– 11.1; – 18.2 (6.2; 1.8)	0.9; 2.9	4.3; – 5.5	5.9; 1.8/ – 1.3; 7.6
β(C_{aryl}-O-$C_{carbonyl}$-OAr)	176.4; 175.8	– 173.6; – 175.1	160.8; 169.9 (– 176.0; – 176.1)	– 178.4; – 177.8	– 176.1; 175.0	– 173.45; – 179.0/ – 171.0; 177.3
γ(C_{aryl}-C_{aryl}-O-$C_{carbonyl}$)	– 108.5, 71.5; 72.5, – 108.3	– 82.3, 99.6; 109.3, – 74.7	– 90.9, 96.1; 78.5, – 103.4 (– 73.5, 105.7; 105.7, – 72.3)	– 115.3, 69.8; 71.5, – 111.4	– 132.8, 53.8; – 58.9, 128.0	– 47.9, 135.5; 89.2, – 93.9/ 89.1, – 96.2; – 102.3, 82.8
$\lvert\delta\rvert$[c]	71.1; 69.9	78.1; 71.3	93.8; 69.6 (79.9; 71.5)	69.1; 67.3	53.0; 58.7	43.2; 91.7/ 79.3; 89.1
ε[d]	71.3	62.4	54.9 (55.0)	50.8	22.4	65.2/44.3
A:B:C[e]	2.8:2.6:1.0	3.0:2.9:1.0	3.2:3.1:1.0 (3.3:3.2:1.0)	3.2:3.1:1.0	–	–

[a] Data belonging to one of the two phenolic moieties are separated by a comma. The data of one phenolic moiety are separated by a semicolon from the corresponding data of the second phenolic moiety of a carbonate. [b] Data of **10** belonging to one or the other carbonate unit are separated by a diagonal stroke. [c] δ is the angle by which the plane of the benzoate ring intersects with the plane given by the three oxygen atoms of the carbonate group. [d] ε is the torsion angle between the planes of the two benzoate rings. [e] The ratio A:B:C describes the ratio of the lengths of the edges of the distorted tetrahedron where A, B, and C are the averaged values of A_1/A_2, B_1/B_2 and C_1/C_2 as defined in Figure 3.

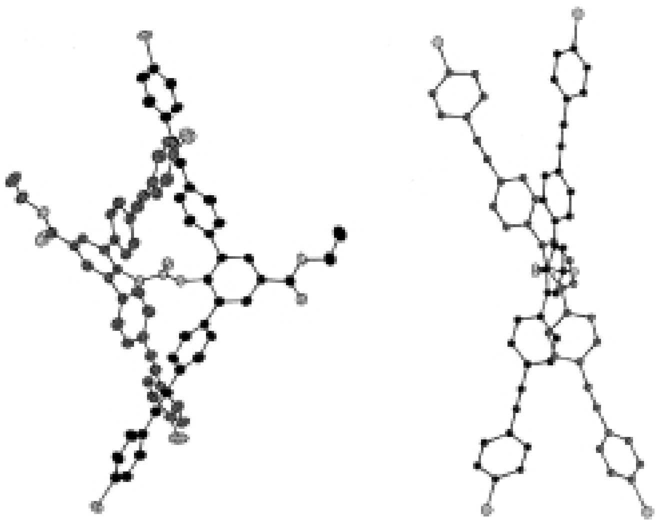


Figure 1. Structure of carbonate **7c** in the crystal (free of solvent). Carbon atoms are shown in black and dark grey except the carbon atom of the carbonyl group which is colourless. Oxygen atoms are shown as small light grey ellipsoids or circles, bromine atoms as large light grey ellipsoids or circles. Left: Ortep plot (50% probability). Right: View along the connecting line between the two C_α-4 atoms. The ester groups have been omitted for clarity.

given by the torsion angle $\alpha(\mathrm{C_{aryl}}\text{-O-}\mathrm{C_{carbonyl}}\text{-}\mathrm{O_{carbonyl}}) = 0.9-18.2^\circ$ (Figures 1 and 2). The significantly different values for α in **7c** (-11.1° and -18.2°) and **7c**$\cdot CH_2Cl_2$ (6.2°and 1.8°) suggest that this torsion angle is strongly influenced by packing effects. The two values for α of the carbonates **5a**, **6c**, **7c** and **8c** are either both positive or both negative. The same is true for the torsion angle $\beta(\mathrm{C_{aryl}}\text{-O-}\mathrm{C_{carbonyl}}\text{-OAr})$. In contrast, the two values for α and the two values for β of carbonate **9** are of opposite sign. The carbonate groups of compound **10** show both possible combinations for α and for β. These data indicate that none of the two possible combinations of the torsion angles α and β is particularly preferred as long as no substituents are present at the phenolic moieties. Substituents, such as those in the 3- and 5-position of the hydroxybenzoate moieties of the carbonates **5**–**8**, result in the preference of the described conformation because otherwise the substituents would be too close to each other. These substituents also influence the torsion angle $\gamma(\mathrm{C_{aryl}}\text{-}\mathrm{C_{aryl}}\text{-O-}\mathrm{C_{carbonyl}})$ and, consequently, the torsion angles δ and ε. The torsion angle δ is the angle at which the plane of the benzoate ring intersects the plane defined by the three oxygen atoms of the carbonate group. The values of δ of the carbonates **5a**, **6c**, **7c** and **8c** are in the range of 67–94°. Smaller values are found in the structures of **9** (53.0° and 58.7°) and **10** (43.2° and 91.7°/79.3° and 89.1°). The torsion angle ε is the angle between the planes of the two benzoate rings of **5**–**8** or the phenyl rings of **9** and **10**. This angle is very small in the structure of **9** (22.4°) compared to that in the structures of the carbonates **5a**, **6c**, **7c** and **8c** (51–71°).

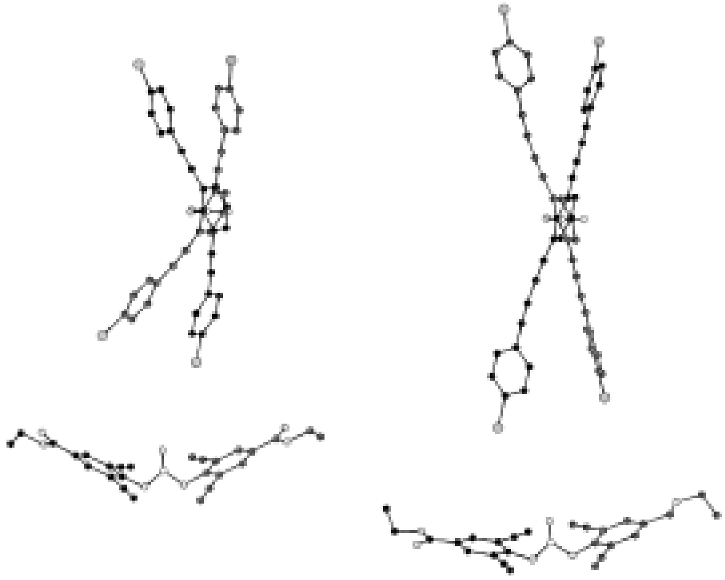


Figure 2. Structure of carbonates **6c**$\cdot CHCl_3$ (left) and **8c**$\cdot CH_2Cl_2$ (right) in the crystal. Solvent molecules are not shown. For the colour key, see Figure 1. Top: View along the connecting line between the two C4 atoms of the hydroxybenzoate units. The ester groups have been omitted for clarity. Bottom: Perpendicular view onto the carbonate plane. The substituents in 3,5-position of the hydroxybenzoate moieties are truncated.

As a result, in all examples, the substituents in the 3- and 5-position of the benzoate moieties point towards the corners of a distorted tetrahedron with the carbonate moiety in the center of the tetrahedron and the two angular phenolic building blocks intersecting with an angle of 51–71°. The degree of distortion is reflected in the ratio $A{:}B{:}C$ (Table 1), with A, B and C being the averaged values for the lengths of the edges A_1/A_2, B_1/B_2 and C_1/C_2 of the tetrahedron (Figure 3). The intersecting or helical arrangement of the two angular phenolic building blocks can be clearly seen in Figure 2 in which the structures of the carbonates **6c** and **8c** are presented viewed along the connecting line between the two C4 atoms of the hydroxybenzoate unit. This intersection results in a chiral structure. Both enantiomers are present in the crystals, as indicated by the centrosymmetry of the space group.

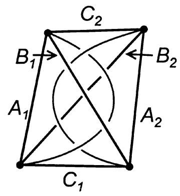


Figure 3. Distorted tetrahedral arrangement of the substituents in the 3,5-position of the benzoate moiety with designation of the edges.

Conformational dynamics in solution: From the molecular structure of carbonates **5**–**8** in the crystal, it is expected that the carbonates in solution show a C_2 symmetry with the C_2 axis coinciding with the carbonyl bond. However, a higher symmetry of the carbonates **5**–**8** in solution at room temperature is revealed by NMR spectroscopy (300 MHz): the four substituents in the 3- and 5-positions of the benzoate moieties are magnetically equivalent and the benzoate rings give rise to only one signal in the ^1H NMR spectrum (300 MHz) and four signals in the ^{13}C NMR spectrum (75 MHz). The symmetry of **6**–**8** is reduced when the temperature is lowered. ^1H NMR spectra (300 MHz; THF) of the carbonates **6c**, **7b**[18] and **8b**[18] at 163 K, 186 K or 163 K, respectively, show two sets of signals for the aromatic protons of the substituents and one (**6c**) or two (**7b** and **8b**) signals for the protons of the benzoate rings (Figures 4–6). In contrast to this, the signals of carbonate **5a** (THF, 300 MHz) at 164 K are significantly broadened, however, they are not split. ^{1}H NMR spectra (300 MHz, THF) of the corresponding phenols **2c**, **3b** and **4b** at these temperatures reveal only a slight broadening of the aromatic signals and some loss of the fine structure of the ethyl groups. Therefore, freezing of the rotation of the phenylene units in the substituents of the hydroxybenzoate moieties is not the reason for the reduced symmetry of the carbonates **6c**, **7b** and **8b** at low temperatures.

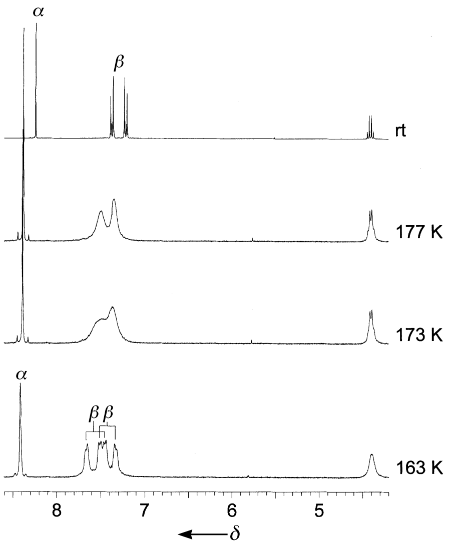


Figure 4. Partial ^{1}H NMR (300 MHz) spectra of carbonate **6c** in [D$_8$]THF. The brackets connect signals that coalesce at higher temperatures. The detailed assignment of signals to H$_\beta$-2,-6 and H$_\beta$-3,-5 is not possible.

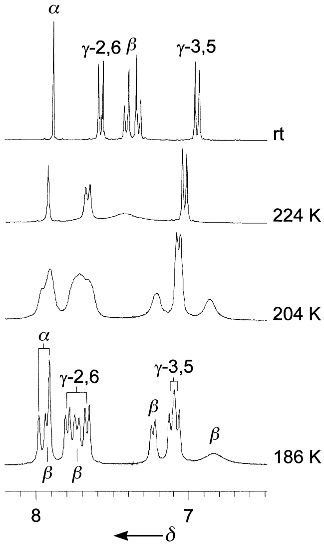


Figure 5. Partial ^{1}H NMR (300 MHz) spectra of carbonate **7b** in [D$_8$]THF. The brackets connect signals that coalesce at higher temperatures. The detailed assignment of signals to H$_\beta$-2,-6 and H$_\beta$-3,-5 is not possible. At low temperatures, the ethyl groups (not shown) become as broad and structureless as seen in the spectra of **8b** (Figure 6).

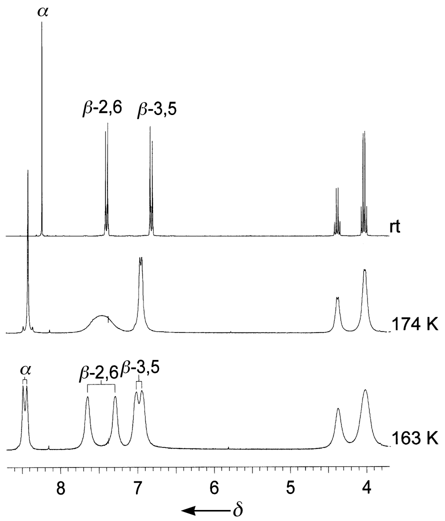


Figure 6. Partial ^{1}H NMR (300 MHz) spectra of carbonate **8b** in [D$_8$]THF. The brackets connect signals that coalesce at higher temperature.

In the further discussions, the following nomenclature will be used (Scheme 1, Figure 7): the aromatic rings are designated with Ar$_\alpha$, Ar$_\beta$ and Ar$_\gamma$ with the hydroxybenzoate moiety being Ar$_\alpha$, the benzene unit closest to the hydroxybenzoate moiety being Ar$_\beta$ and the residual benzene unit being Ar$_\gamma$. To distinguish further, the aromatic rings Ar$_\beta$ and Ar$_\gamma$ that belong to the same angular phenolic unit of the carbonate are marked with superscripts 1 and 2 or 3 and 4, for example ^{1}Ar$_\beta$ and ^{2}Ar$_\beta$ or ^{3}Ar$_\beta$ and ^{4}Ar$_\beta$. For the numbering of the positions, the ethyl 4-hydroxybenzoate is considered as the substituted parent compound.

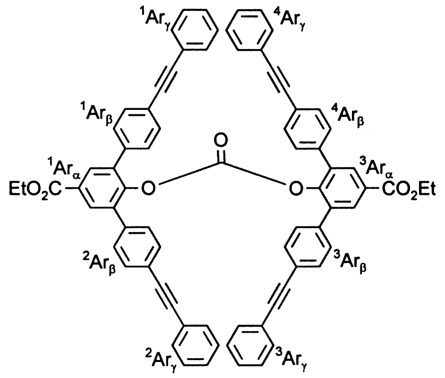


Figure 7. The designation of the benzene rings of the carbonates **5**–**8**.

In order to correlate the observed molecular dynamics with specific conformational changes, the coalescence temperatures T_c for all aromatic signals were determined and the energy barrier $\Delta G_c^{\neq}$ was calculated according to Equation (1).[19]

$$\Delta G_c^{\neq} = 4.57\, T_c (9.97 + \log T_c - \log \Delta\nu) \qquad (1)$$

where $\Delta\nu$ is the shift difference of the exchanging protons at the limit of no exchange. Complete freezing of the dynamics may not have been reached in all of our experiments. Therefore, for $\Delta\nu$ we used the maximum shift difference observed. The signal assignment for **6c**, **7b** and **8b** is in accordance with H,H-COSY spectra at 163 K, 160 K or 177 K, respectively. The results are summarized in Table 2. The two or three values of $\Delta G_c^{\neq}$ obtained for one carbonate are very similar or even identical. Thus, it is assumed that the splitting of the signals resembles the slowing down of just one specific dynamic process.

Table 2. Kinetic and thermodynamic data for carbonates **6**–**8** in [D$_8$]THF obtained from temperature-dependent ^{1}H NMR spectroscopy (300 MHz).

		$\Delta\nu$ [Hz]	T_c [K]	$\Delta G_c^{\neq}$ [kcal mol^{-1}]
6c	H_β-3,-5 or H_β-2,-6	61	173	8.2
	H_β-2,-6 or H_β-3,-5	54	172	8.2
7b[a]	H_α	21	206	10.3
	H_γ-2,-6	38	206	10.1
	H_γ-3,-5	16	198	10.0
8b	H_α	15	166	8.3
	H_β-2,-6	107	175	8.1
	H_β-3,-5	21	166	8.2

[a] A detailed assignment of signals to H_β-2,-6 or H_β-3,-5 is not possible.

To explain the number of signals at low temperatures, two cases are possible: a) The magnetic equivalence found at room temperature for the two tolane substituents on the same benzoate ring is lost upon cooling, that is, the magnetic equivalence of the rings $^1Ar_\beta$ and $^2Ar_\beta$, $^1Ar_\gamma$ and $^2Ar_\gamma$, $^3Ar_\beta$ and $^4Ar_\beta$, $^3Ar_\gamma$ and $^4Ar_\gamma$ is lost, while the two angular phenolic building blocks are still related by C_2 symmetry, namely $^1Ar_\beta$ and $^3Ar_\beta$, $^2Ar_\beta$ and $^4Ar_\beta$, $^1Ar_\gamma$ and $^3Ar_\gamma$, $^2Ar_\gamma$ and $^4Ar_\gamma$ are magnetically equivalent. b) The two tolane substituents of the same benzoate ring remain magnetically equivalent, namely $^1Ar_\beta$ and $^2Ar_\beta$, $^1Ar_\gamma$ and $^2Ar_\gamma$, $^3Ar_\beta$ and $^4Ar_\beta$, $^3Ar_\gamma$ and $^4Ar_\gamma$ are magnetically equivalent, while the symmetry relationship between the two angular phenolic building blocks is lost, namely $^1Ar_\beta$ and $^3Ar_\beta$, $^2Ar_\beta$ and $^4Ar_\beta$, $^1Ar_\gamma$ and $^3Ar_\gamma$, $^2Ar_\gamma$ and $^4Ar_\gamma$ are magnetically not equivalent. For case (a) coupling between the protons H_α-2 and H_α-6 is expected while for case (b) no coupling is expected. The H,H-COSY 45 spectrum of carbonate **7b** at 177 K (300 MHz, Figure 8) shows cross-peaks for the two signals of H_α which is in accordance with case (a). The H,H-COSY 90 spectrum of **8b** at 163 K (300 MHz, not shown) also shows cross-peaks for the two signals of H_α. However, in the latter case, additional cross-peaks for the two signals of H_β-2,-6 and for the two signals of H_β-3,-5 are found, albeit of comparably very low intensity. This means that at 163 K, the dynamics of **8b** are not sufficiently slow to avoid cross-peaks because of the transfer of magnetisation through conformational exchange. Hence the reason for the cross-peaks for the two signals of H_α is arguable and the result of the H,H-COSY 90 experiment with carbonate **8b** (163 K) does not allow for a definite decision for either case (a) or (b). On the other hand, the result of the H,H-COSY 90 experiment with carbonate **8b** is in accordance with the conclusion drawn from the H,H-COSY 45 experiment on carbonate **7b** (177 K): upon lowering the temperature, the symmetry within the angular phenolic building blocks of the carbonate is broken while the symmetry relationship between the two angular phenolic building remains [case (a)].

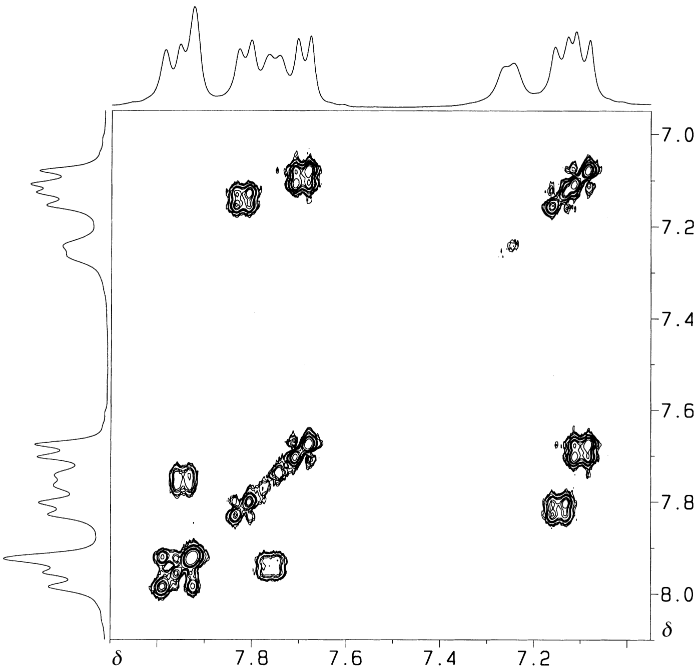


Figure 8. Partial H,H-COSY 45 spectrum (300 MHz) of carbonate **7b** in [D$_8$]THF at 177 K. A total of 256 spectra, each consisting of 2048 data points over the width of 3 ppm, were accumulated with 8 scans for each t_1. The data were calculated with SI(F2) = 1024 and SI(F1) = 512 and with the sine function for both directions. The spectra at the axes were obtained immediately after COSY data accumulation at the same temperature.

The symmetry of the carbonates in solution at low temperatures, derived from NMR spectroscopy, fits to the molecular structure of the carbonates in the crystalline state. It is assumed that the two enantiomeric structures in the crystalline state resemble the preferred conformations of the carbonates in solution at low temperatures. Knowing the molecular structure of the carbonates in solution at low temperatures enables us to draft pathways of conformational changes that lead to the observed high symmetry of the carbonates at room temperature. One possibility is the interconversion of the two enantiomeric conformers present in the crystal by coupled, small rotations around the $C_{aryl}-O$ and $C_{carbonyl}-OAr$ bonds with a transitional, perfect *trans* conformation in which C_α-4 and all atoms of the carbonate unit lie in one plane and the plane of the Ar_α is perpendicular to the carbonate plane. This appears feasible only for carbonate **5a**. In the case of carbonate **6c**, the substituents are already too long to pass each other. This steric problem becomes obvious on viewing carbonates **5a** and **6c** along the carbonyl bond (Figure 9). A dynamic process that can explain the equivalence of all four substituents of the carbonates **6**–**8** is sketched in Scheme 2a. The drawings show schematically the carbonates viewed along the carbonyl bond with the oxygen atom pointing towards the reader. Essentially, they describe a continuous rotation of the angular building blocks (π flip) around the carbonate unit with the $C_{aryl}-O$ bonds as the axes of rotation. The deviation from a perfectly planar W shape at the carbonate moiety is neglected for clarity. A rapid interconversion of all four structures in Scheme 2a leads to the observed symmetry. Taking into account that the rotation around $C_{aryl}-O$ is hindered by the carbonyl oxygen,[2, 4] it is

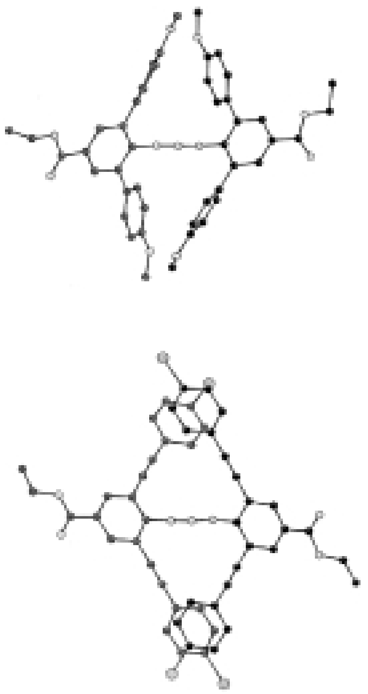
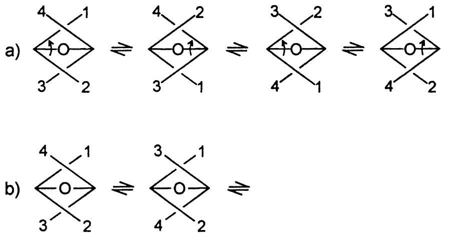


Figure 9. Structure of carbonates **5a** (top) and **6c**·$CHCl_3$ (bottom) in the crystal viewed along the carbonyl bond with the oxygen atom pointing towards the reader. Solvent molecules are not shown. For the colour key, see Figure 1.



Scheme 2. Dynamic conformational process for carbonates **6**–**8**.

assumed that this conformational interconversion is better described by a combination of large changes in the torsion angles $\alpha(C_{aryl}\text{-}O\text{-}C_{carbonyl}\text{-}O_{carbonyl})$ and $\gamma(C_{aryl}\text{-}C_{aryl}\text{-}O\text{-}C_{carbonyl})$ of one of the two angular building blocks.[2, 6] As α increases, the rotation around C_{aryl}–O becomes less hindered by the carbonyl oxygen. In a transitional structure, α may be $\approx 90°$ and the plane of the benzoate ring may be nearly coplanar with the ArO–$C_{carbonyl}$ bond. The other angular building block of the carbonate has to undergo only small adjustments by rotations around the ArO–$C_{carbonyl}$ and C_{aryl}–O bonds, in a similar manner to those described for carbonate **5a**. In the next rotation, the roles of the two angular building blocks are exchanged.

The rotational barriers in carbonate **10** and the corresponding poly(bisphenol A carbonate) has been the subject of several calculations with the aim of correlating the macroscopic material properties of polycarbonates, such as the impact resistance, with conformational dynamics.[3, 4, 6] Very little is known about substituted derivatives.[4, 8] A short note[4] offers some insight as to how substituents influence the rotation barriers: for carbonate **10** the barrier for rotation around the C_{aryl}–O bond was calculated to be 1.2 kcal mol^{-1}[2, 4] to 3.3 kcal mol^{-1}.[6] Substitution of the phenols in the *ortho* position to the oxygen substituent by methyl or ethyl groups, raised the rotation barrier to 5.0 and 7.5 kcal mol^{-1}, respectively, in the case that the methyl or ethyl substituent passed the carbonyl group.[4] Two methyl substituents at the phenol in the *ortho* position with respect to the oxygen substituent, resulted in a rotation barrier of 7.9 kcal mol^{-1}.[4] The barrier of the rotation around the $C_{carbonyl}$–OAr bond in carbonate **10** was calculated to be 4 kcal mol^{-1}[6] to 8.7 kcal mol^{-1}.[2] The experimentally determined activation energies $\Delta G_c^{\neq}$ for carbonates **6**–**8** (8–10 kcal mol^{-1}) agree well with these calculated data and thus support the assumption of the conformational interconversion process shown in Scheme 2a.

An alternative process is the exchange of the two substituents of the same benzoate unit. This is illustrated in Scheme 2b with two of the possible structures. If the four substituents were different, this process would result in racemisation. In contrast to this, the process shown in Scheme 2a would not produce a racemate. The path of interchange in Scheme 2b appears to be very unlikely because it requires a cooperative change of several torsion angles and rather unfavourable, intermediate conformations at the carbonate group to circumvent steric problems with the substituents and to avoid unfavourable interaction between the substituents and the oxygen atom of the carbonyl group. The pathway shown in Scheme 2a should require distinctly lower energy.

The energy barrier for the π flip according to Scheme 2a is mainly attributed to the interaction of the carbonyl oxygen with the ethynylene units or with Ar_β. Therefore, the energy barriers for the π flip in carbonates **5a** and **7b** should be very similar. No such barrier was found for carbonate **5a**. This leads to the conclusion that the molecular symmetry of carbonate **5a** in solution is not reached by π flips, but as described above, by small rotations around the C_{aryl}–O and $C_{carbonyl}$–OAr bonds with a transitional, perfect *trans* conformation in which C_α-4 and all atoms of the CO_3 unit lie in one plane and in which the plane of the Ar_α is perpendicular to the carbonate plane. This is, to our knowledge, the first experimental proof of this kind of conformational interconversion which has been predicted by calculations and is discussed as the reason for the γ relaxation process in polycarbonates.[3]

Conclusions

The carbonates **5**–**8** were prepared from the corresponding 4-hydroxyphenolates and triphosgene. For the carbonates **5** and **6** pyridine is sufficient as the base. For high yield of carbonates **7** and **8**, sodium hydride is necessary as the base. The carbonate unit of **6** and **8** was cleaved by pyridine and DMAP, while the carbonate unit of **5** and **7** proved to be rather inert under these conditions.

The structures of carbonates **5**–**8** in the crystal show a *trans*, *trans* or W-shaped conformation at the C_{aryl}-O-CO-O-C_{aryl} unit with small deviations from a planar W. They are characterized by the intersection of the two angular phenolic moieties at an angle of 50–71°. In solution conformational mobility at room temperature makes the four substituents of the hydroxybenzoate magnetically equivalent. In the case of carbonates **6**–**8**, this process requires 8–10 $kcal\,mol^{-1}$. It can be described essentially as a continuous rotation of the angular phenolic moieties around the carbonate unit with the $C_{aryl}-O$ bonds as the axes of rotation. Carbonate **5** follows another, energetically less demanding, route via a perfect *trans* conformation in which the plane of the Ar_α is perpendicular to the carbonate plane.

An efficient synthesis of [2]catenanes from two acyclic molecules or from one acyclic and one cyclic molecule requires a suitable preorganisation of these building blocks.[20] The investigations on the carbonates **5**–**8** suggest carbonates like **6**–**8** as covalent templates for the catenane synthesis. Although the carbonate group is conformationally flexible, the two angular phenolic moieties are always intersecting. Therefore, the experimentally found formation of a mixture of entwined and non-entwined rings[1] is attributed to the conformational flexibility of the huge rings and not to geometrical ambiguity of the carbonate linkage.

Experimental Section

Crystal structure analysis: Table 3 provides a summary of the relevant data concerning the crystal structure analysis. Data of **5a** and **6c** were collected on a Nonius CAD4 diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). The lattice parameters were obtained from a least-squares analysis of the setting angles of 25 reflections with $\theta > 20°$. Data collection was carried out by $\theta - 2\theta$ scans. An empirical absorption correction was applied. The data of **7c** and **8c** were collected on a Nonius KCCD detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7103$ Å). No absorption correction was applied. The structures of **6c**, **7c** and **8c** were solved by heavy atom methods, the structure of **5a** was solved by direct methods (SHELXS). The structures were refined by full-matrix least-squares analysis on *F* (unit weights) with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode.

General: All reactions were performed under an inert atmosphere. THF was distilled from sodium/benzophenone. Pyridine was dried over CaH_2. The starting compounds **1**–**4** were synthesized as described in the literature.[21] Triphosgene was purchased from Aldrich and used without further purification. The petroleum ether used had a boiling range of 30–40 °C. Flash chromatography was carried out on Merck silica gel (40–63 µm) and TLC on aluminum foils coated with silica gel (Merck alumina foils $60\,F_{254}$). Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ as the solvent and internal standard on a Bruker AMX-300 MHz at room temperature. For signal assignment, the carbon multiplicity was determined by a DEPT experiment. The subscripts α, β, and γ refer to the aromatic rings, as explained in the text and in Scheme 1. The melting points were determined in open capillaries.

5a: To a cooled (ice bath) solution of phenol **1a** (291 mg, 0.77 mmol) in THF (5 mL) were successively added triphosgene (38 mg, 0.128 mmol) and pyridine (0.1 mL, 1.2 mmol). A colourless precipitate formed immediately. The suspension was stirred at room temperature for 3 d and then it was cooled (ice bath) and hydrolysed with 1N HCl. After diluting with water, the precipitate was filtered off and dried in vacuo over P_4O_{10}. The colourless solid was suspended twice in refluxing ethanol (35 mL and 50 mL, respectively) to remove residual **1a**. Carbonate **5a** (200 mg, 61 %) was obtained as a colourless solid. Crystals for X-ray structure analysis were prepared by recrystallisation from ethanol. M.p. 200.7 °C; ^1H NMR: $\delta = 7.83$ (s, 4H; H_α), 7.21 (half of AA′XX′, 8H; H_β-2,-6), 6.74 (half of AA′XX′, 8H; H_β-3,-5), 4.32 (q, $J = 7$ Hz, 4H; CH_2), 3.86 (s, 12H; OCH_3), 1.32 (t, $J = 7$ Hz, 6H; CH_2CH_3); ^{13}C NMR: $\delta = 165.7$ (CO_2), 159.1 (C_β-4), 147.5, 147.4 (C_α-4, CO_3), 135.4 (C_α-3,-5), 131.2 (C_α-2,-6) 129.9 (C_β-2,-6), 128.9 (C_β-1), 128.8 (C_α-1), 113.9 (C_β-3,-5), 61.1 (CH_2), 55.2 (OCH_3), 14.3 (CH_2CH_3); elemental analysis calcd (%) for $C_{47}H_{42}O_{11}$ (782.842): C 72.11, H 5.41; found: C 72.11, H 5.46.

6c: To a cooled (ice bath) solution of phenol **2c** (430 mg, 0.82 mmol) in THF (10 mL) were successively added triphosgene (41 mg, 0.138 mmol) and pyridine (0.2 mL, 2.5 mmol). A colourless precipitate formed immediately. The suspension was stirred at room temperature for 16 h and then it was cooled (ice bath) and hydrolysed with 0.1N HCl. The brown precipitate was filtered off and washed with water. ^1H NMR spectroscopy of the crude product (432 mg) showed the conversion to be 91 %. After drying (P_4O_{10}/vacuum), the solid was dissolved in CH_2Cl_2 (3 mL) and carbonate **6c** (259 mg, 56 %) was isolated as a colourless powder by the addition of diethyl ether. Crystals for X-ray structure analysis were obtained by slow diffusion (via the gas phase) of diethyl ether into a solution of carbonate **6c** in $CHCl_3$. M.p. 192 °C; ^1H NMR: $\delta = 8.21$ (s, 4H; H_α), 7.26, 7.11 (AA′XX′, 8H each; H_β), 4.43 (q, $J = 7$ Hz, 4H; CH_2), 1.43 (t, $J = 7$ Hz, 6H; CH_3); ^{13}C NMR: $\delta = 164.4$ (CO_2Et), 153.5 (C_α-4), 147.6 (CO_3), 134.2 (C_α-2,-6), 133.1 (C_β-2,-6), 131.2 (C_β-3,-5), 129.4 (C_α-1), 123.3 (C_β-4), 120.7 (C_β-1), 118.5 (C_α-3,-5), 95.6, 83.3 ($C\equiv C$), 61.8 (CH_2), 14.3 (CH_3); elemental analysis calcd (%) for $C_{51}H_{30}Br_4O_7$ (1074.434): C 57.01, H 2.81; found: C 57.44, H 3.17.

7b: As described for the preparation of **8b**, carbonate **7b** was prepared from phenol **3b** (1.00 g, 1.64 mmol) with triphosgene (81 mg, 0.275 mmol; added as a solid) and NaH (60 % dispersion in mineral oil; 72 mg, 1.80 mmol), in THF (20 mL). After 17 h at room temperature, the reaction mixture was hydrolysed with 2N HCl and extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Conversion of 97 % was determined by ^1H NMR spectroscopy of the crude product. Flash chromatography (petroleum ether/CH_2Cl_2 1:4, $R_f = 0.67$) gave carbonate **7b** (850 mg, 82 %) as a colourless solid. Single crystals for X-ray structure analysis were obtained by slow diffusion (via the gas phase) of ethanol into a solution of **7b** in toluene/acetone. M.p. 143.3 °C; ^1H NMR:

Table 3. Relevant data concerning the crystal structure analysis of carbonates **5**–**8**.

	5a	**6c**·$CHCl_3$	**7c**	**7c**·CH_2Cl_2	**8c**·CH_2Cl_2
a [Å]	17.5400(9)	25.3514(6)	14.3034(6)	17.5849(9)	14.750(1)
b [Å]	18.900(2)	18.4229(7)	14.8360(6)	18.823(1)	15.295(1)
c [Å]	24.9581(7)	24.3276(6)	17.6839(5)	20.417(1)	14.828(1)
α [°]	90	90	66.760(2)	90	90.687(5)
β [°]	90	117.991(5)	70.730(2)	99.292(4)	102.270(5)
γ [°]	90	90	62.601(2)	90	116.694(5)
lattice type	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
V [Å^3]	8273.9	10033	3010.3(2)	6669.4(4)	2898.2
Z	8	8	2	4	2
ρ_{calcd} [$g\,cm^{-3}$]	1.257	1.425	1.521	1.458	1.452
μ [mm^{-1}]	0.697	4.328	2.703	2.523	2.885
space group	*Pbca*	*C2/c*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
T [K]	RT	RT	195	195	RT
no. reflns	–	–	20610	25260	–
no. unique reflns measured	6386	6635	13623	8422	7887
no. unique reflns observed	3431	3271	5837	4254	3728
R_{int}	–	–	0.023	0.03	–
R	0.0437	0.0463	0.0338	0.068	0.0487
R_w	0.0412	0.0608	0.0395	0.089	0.0626
λ	$Cu_{K\alpha}$	$Cu_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
θ_{max}	58	60	27.5	27.5	27.5

0947-6539/00/0619-3528 $ 17.50+.50/0

$\delta = 7.88$ (s, 4H; H$_{\alpha}$), 7.58 (half part of AA′XX′, 8H; H$_{\gamma}$-2,-6), 7.39, 7.30 (AA′XX′, 8H each; H$_{\beta}$), 6.89 (half part of AA′XX′, 8H; H$_{\gamma}$-3,-5), 4.32 (q, $J = 7$ Hz, 4H; CO_2CH_2), 4.07 (q, $J = 7$ Hz, 8H; $ArOCH_2$), 1.44 (t, $J = 7$ Hz, 12H; $ArOCH_2CH_3$), 1.32 (t, $J = 7$ Hz, 6H; $CO_2CH_2CH_3$); ^{13}C NMR: $\delta =$ 165.3 (CO_2), 159.1 (C$_{\gamma}$-4), 147.6 (CO_3), 147.1 (C$_{\alpha}$-4), 135.6, 135.4 (C$_{\beta}$-1, C$_{\alpha}$-3,-5), 133.2 (C$_{\gamma}$-2,-6), 131.72, 131.66 (C$_{\alpha}$-2,-6, C$_{\beta}$-3,-5), 129.2 (C$_{\alpha}$-1), 128.6 (C$_{\beta}$-2,-6), 123.3 (C$_{\beta}$-4), 115.4 (C$_{\gamma}$-1), 114.6 (C$_{\gamma}$-3,-5), 90.7 ($C{\equiv}CAr_{\gamma}$), 88.3 ($Ar_{\beta}C{\equiv}C$), 63.5 ($ArOCH_2$), 61.3 (CO_2CH_2), 14.7 ($ArOCH_2CH_3$), 14.3 ($CO_2CH_2CH_3$); elemental analysis calcd (%) for $C_{83}H_{66}O_{11}$ (1239.430): C 80.43, H 5.37; found: C 80.07, H 5.06.

7c: As described for the preparation of **8b**, carbonate **7c** was prepared from phenol **3c** (338 mg, 0.50 mmol) with NaH (60% dispersion in mineral oil; 22 mg, 0.55 mmol) and triphosgene (24.7 mg, 0.083 mmol; added as a solid) in THF (10 mL). After 5 h at room temperature, the reaction mixture was hydrolysed with 2N HCl and extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The conversion was determined by ^1H NMR spectroscopy of the crude product to be 94%. Flash chromatography (petroleum ether/CH_2Cl_2 1:2, $R_f = 0.28$) gave carbonate **7c** (310 mg, 91%) as a colourless solid. Recrystallisation from CH_2Cl_2/ethanol gave needlelike and cube-shaped crystals. The needles were free of solvent, the cubes contained CH_2Cl_2. M.p. 318.0–319.8 °C; ^1H NMR: $\delta = 7.88$ (s, 4H; H$_{\alpha}$), 7.51, 7.46 (AA′XX′, 8H each; CH$_{\gamma}$), 7.39, 7.31 (AA′XX′, 8H each; CH$_{\beta}$), 4.33 (q, $J = 7$ Hz, 4H; CO_2CH_2), 1.32 (t, $J = 7$ Hz, 6H; CH_3); ^{13}C NMR: $\delta = 165.2$ (CO_2), 147.7 (CO_3), 147.1 (C$_{\alpha}$-4), 136.2, 135.2 (C$_{\beta}$-1, C$_{\alpha}$-3,-5), 133.0 (C$_{\gamma}$-2,-6), 131.9, 131.8, 131.7 (C$_{\alpha}$-2,-6, C$_{\gamma}$-3,-5, C$_{\beta}$-3,-5), 129.4 (C$_{\alpha}$-1), 128.7 (C$_{\beta}$-2,-6), 122.7, 122.5, 122.2 (C$_{\beta}$-4, C$_{\gamma}$-1, C$_{\gamma}$-4), 90.6 ($C{\equiv}CAr_{\gamma}$), 89.6 ($Ar_{\beta}C{\equiv}C$), 61.4 (CO_2CH_2), 14.3 (CH_3); elemental analysis calcd (%) for $C_{75}H_{46}O_6Br_4$ (1362.827): C 66.09, H 3.40; found: C 65.64, H 3.51.

8b: Sodium hydride (60% dispersion in mineral oil; 140 mg, 3.5 mmol) was suspended in THF (2 mL). After the NaH had deposited, the solvent was removed using a pipette. The flask was immersed in an ice bath. To the residual NaH were added successively THF (10 mL), phenol **4b** (695 mg, 1.38 mmol) and triphosgene (7.5 mL (0.23 mmol) of a solution of triphosgene (365 mg) in THF (40 mL)). After 26 h at room temperature, the reaction mixture was hydrolysed with 2N HCl under cooling (ice bath) and extracted with diethyl ether. The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. ^1H NMR spectroscopy of the crude product showed the conversion to be 93%. The solid brown residue was dissolved in CH_2Cl_2 (8 mL) and the carbonate **8b** (485 mg, 65%) was precipitated by the addition of diethyl ether (50 mL). The precipitate contained about 1% of starting material **4b**. M.p. 217.9 °C; ^1H NMR: $\delta = 8.21$ (s, 4H; H$_{\alpha}$), 7.34 (half of AA′XX′, 8H; H$_{\beta}$-2,-6), 6.73 (half of AA′XX′, 8H; H$_{\beta}$-3,-5), 4.37 (q, $J = 7$ Hz, 4H; CO_2CH_2), 4.00 (q, $J = 7$ Hz, 8H; $ArOCH_2$), 1.40 (t, $J = 7$ Hz, 12H; $ArOCH_2CH_3$), 1.38 (t, $J = 7$ Hz, 6H; $CO_2CH_2CH_3$); ^{13}C NMR: $\delta = 164.2$ (CO_2Et), 159.9 (C$_{\beta}$-4), 155.3 (C$_{\alpha}$-4), 147.6 (CO_3), 135.3 (C$_{\alpha}$-2,-6), 134.3 (C$_{\beta}$-2,-6), 129.3 (C$_{\alpha}$-1), 118.2 (C$_{\alpha}$-3,-5), 114.5 (C$_{\beta}$-3,-5), 113.3 (C$_{\beta}$-1), 84.4, 81.6 ($C{\equiv}C{-}C{\equiv}C$), 73.1, 72.8 ($C{\equiv}C{-}C{\equiv}C$), 63.6 ($ArOCH_2$), 61.7 (CO_2CH_2), 14.7 ($ArOCH_2CH_3$), 14.2 ($CO_2CH_2CH_3$); elemental analysis calcd (%) for $C_{67}H_{50}O_{11}$ (1031.126): C 78.04, H 4.89; found: C 78.12, H 5.08.

8c: As described for the preparation of **8b**, carbonate **8c** was prepared from phenol **4c** (158 mg, 0.28 mmol) with NaH (60% dispersion in mineral oil; 80 mg, 2.0 mmol) and triphosgene (1.5 mL (0.046 mmol) of a solution of triphosgene (365 mg) in THF (40 mL)) in THF (8 mL). After 20 h at room temperature, the reaction mixture was hydrolysed with 2N HCl under cooling (ice bath) and extracted with diethyl ether/THF. The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. ^1H NMR spectroscopy of the crude product showed the conversion to be 92%. The residue was dissolved in CH_2Cl_2 (2 mL) and the carbonate **8c** (100 mg, 62%) was precipitated by the addition of petroleum ether. The precipitate contained about 2% of starting material **4c**. Yellow needles for X-ray structure analysis were obtained by slow diffusion (via the gas phase) of petroleum ether into a solution of carbonate **8c** in CH_2Cl_2. M.p. 236.1 °C (decomp); ^1H NMR: $\delta = 8.26$ (s, 4H; H$_{\alpha}$), 7.38, 7.22 (AA′XX′, 8H each; H$_{\beta}$), 4.39 (q, $J = 7$ Hz, 4H; CH_2), 1.40 (t, $J = 7$ Hz, 6H; CH_3); ^{13}C NMR: $\delta = 163.9$ (CO_2Et), 155.4 (C$_{\alpha}$-4), 147.6 (CO_3), 135.8 (C$_{\alpha}$-2,-6), 133.9 (C$_{\beta}$-2,-6), 131.7 (C$_{\beta}$-3,-5), 129.6 (C$_{\alpha}$-1), 124.1 (C$_{\beta}$-4), 120.2 (C$_{\beta}$-1), 117.8 (C$_{\alpha}$-3,-5), 82.8, 80.8 ($C{\equiv}C{-}C{\equiv}C$), 74.9, 74.1 ($C{\equiv}C{-}C{\equiv}C$), 61.9 (CH_2), 14.2 (CH_3); elemental analysis calcd (%) for $C_{59}H_{30}Br_4O_7$ (1170.522): C 60.54, H 2.58, Br 27.31; found: C 60.78, H 2.91, Br 24.46.

Reaction of carbonates with pyridine: The solution of carbonate in pyridine ($\leq$0.01M) was stirred at room temperature. After the specified reaction times, a small quantity of the solution was poured onto 2N HCl/diethyl ether. Some THF was added. The organic phase was washed with 2N HCl containing NaCl, dried (Na_2SO_4), and the solvent was removed in vacuo.

Reaction of carbonates with DMAP: To a solution of carbonate **8b** or **7b** in THF was added DMAP (6 and 50 molar equivalents, respectively). After the specified time, the reactions were worked up as described for the reaction of carbonates with pyridine.

Acknowledgements

We thank J. Thiel and K. Klimke for the preparation of starting materials, P. Kindervater and Dr. M. Wagner for help with the 2D NMR experiments, and S. Duda for FD mass spectra.

---

[1] Ö. Ünsal, A. Godt, *Chem. Eur. J.* **1999**, *5*, 1728.

[2] B. Montanari, P. Ballone, R. O. Jones, *Macromolecules* **1998**, *31*, 7784.

[3] J. T. Bendler, *Comp. Theor. Polym. Sci.* **1998**, *8*, 83.

[4] J. T. Bendler, J. C. Schmidhauser, *Polym. Prepr.* **1995**, *36(2)*, 55.

[5] M. Tomaselli, M. M. Zehnder, P. Robyr, C. Grob-Pisano, R. R. Ernst, U. W. Suter, *Macromolecules* **1997**, *30*, 3579.

[6] M. Hutnik, A. S. Argon, U. W. Suter, *Macromolecules* **1991**, *24*, 5956, 5970, and references therein.

[7] P. M. Henrichs, H. R. Luss, R. P. Scaringe, *Macromolecules* **1989**, *22*, 2731.

[8] J. F. O'Gara, S. G. Desjardins, A. A. Jones, *Macromolecules* **1981**, *14*, 64.

[9] L. Cotarca, P. Delogu, A. Nardelli, V. Šunjic, *Synthesis* **1996**, 553.

[10] The preparation of an oligocarbonate with 2-phenylethynyl as substituents in the *ortho* positions with respect to the CO_3 substituent by aryl–alkynyl coupling of phenylethyne with a preformed, bromo-substituted oligocarbonate has been reported recently: A. B. Morgan, J. M. Tour, *Macromolecules*, **1998**, *31*, 2857.

[11] H. Eckert, B. Forster, *Angew. Chem.* **1987**, *99*, 922; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 894.

[12] On working with the combination sodium phenolate/diphosgene, we found the following: if diphosgene is added first to a suspension of sodium hydride in THF followed by ethyl 4-hydroxybenzoate, no gas evolution was observed when the phenol was added. Aqueous work-up gave mainly the starting material ethyl 4-hydroxybenzoate. On the other hand, if the phenol was added first to the suspension of sodium hydride (1.5 equiv), the expected gas evolution was observed. Addition of diphosgene followed by aqueous work-up gave the crude product containing mainly (97%) carbonate, although the excess of NaH had not been removed prior to the addition of diphosgene. Furthermore, the preparation of chloroformates with phosgene by the addition of a phenol to the suspension of phosgene/NaH/THF failed. Gas evolution was not observed. If someone has an explanation for this observation, we would highly appreciate it if he would share it with us.

[13] The reaction of carbonates derived from phenols with strongly electron-withdrawing substituents (NO_2 or several F) with pyridine or DMAP has been reported: D. J. Brunelle, *Tetrahedron Lett.* **1982**, *23*, 1739; H. Han, K. D. Janda, *J. Am. Chem. Soc.* **1996**, *118*, 2539.

[14] Crystallographic data for the carbonates **5a**, **6c**, **7c** and **8c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141326 (**5a**), 141327 (**6c** · $CHCl_3$), 141328 (**7c**), 141329 (**7c** · CH_2Cl_2) and 141330 (**8c** · CH_2Cl_2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] J. A. King, Jr., G. Bryant, Jr., *Acta Crystallogr. Sect. C* **1993**, *49*, 550.

[16] 4,4′-Isopropylidenediphenylbis(phenylcarbonate): S. Perez, R. P. Scaringe, *Macromolecules* **1987**, *20*, 68.

[17] We use the words "*cis*" and "*trans*" according to their use in the carbonate literature (e.g. ref. [16]), that is not obeying the Cahn–Ingold–Prelog rules.

[18] The carbonates **7b** and **8b** were used for the dynamic measurements instead of the carbonates **7c** and **8c** because of better solubility and especially because of the larger differences in the chemical shift of the aromatic signals. The structures of **7b** and **8b** in the crystal are expected to be very similar to those found for **7c** and **8c**. Preliminary data for **7b** indicate that this assumption is correct. However, the quality of the crystals was not sufficient owing to a disorder of some of the ethoxyphenyl moieties.

[19] H. Günther, *NMR-Spektroskopie*, Thieme, Stuttgart, **1973**.

[20] See, for example: C. O. Dietrich-Buchecker, J. P. Sauvage, *Chem. Rev.* **1987**, *87*, 795; D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725.

[21] A. Godt, Ö. Ünsal, M. Roos, *J. Org. Chem.* **2000**, *65*, 2837. Compound **3c** was prepared in analogy to **3b**; M.p. 252.3–253.3 °C; elemental analysis calcd (%) for $C_{37}H_{24}O_3Br_2$ (676.416): C 65.70, H 3.58; found: C 65.66, H 3.60.

Received: March 9, 2000 [F2353]