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Single-Crystal Structures of Model Compounds for Poly(2,5-dialkoxy-1,4-phenylenevinylene)

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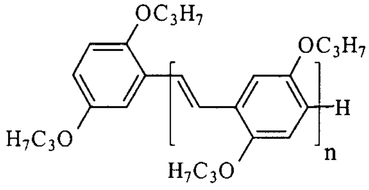
We report on the crystal structures of two alkoxy-substituted distyrylbenzene derivatives **4** and **5** which serve as model compounds for poly(1,4-phenylenevinylene)s and compare them to other known compounds **6**−**9** of similar structure. The obtained data are also related to two alkoxy-substituted stilbene derivatives **2** and **3** to recognize trends of torsion at the olefinic double bonds which are induced by substituents. Surprisingly, the direct impact of substituents on the torsion angles is negligible in comparison to crystal lattice effects. In contrast to quantum mechanical predictions, neither of the compounds **2**−**5** shows in the solid-state weak hydrogen bonding between the oxygen of the alkoxy side chains and the olefinic hydrogens.

Introduction

Ever since the precursor route for the preparation of poly(1,4-phenylenevinylene)s (PPV) was introduced by Wessling,[1] interest in these conjugated polymers has steadily increased because of the possibility to produce suitable thin film devices for the use in light-emitting diodes (LEDs),[2−5] nonlinear optics,[6,7] photoconductors,[8,9] photovoltaics[10,11] or as lasing materials.[12−15] By the introduction of substituents, for example alkyl, aryl, alkoxy, or cyano groups in the phenylene or the vinylene building blocks the processability as well as physical properties such as color of the absorbed or emitted light, conductivity, etc. can be altered over a broad range.[16−21]

The conformational variety in oligo- and poly(1,4-phenylenevinylene)s[22] has on the other hand a decisive influence on the properties. The convergence of the absorption maxima as well as of the fluorescence maxima in the series of oligo(1,4-phenylenevinylene)s such as **1** is essentially determined by conformational effects. Ideally planar OPVs would exhibit such limits of convergence, too, but torsions around the single bonds along the conjugated chain strongly reduce the effective conjugation length.[23] Thus, the point in question is: How do substituents affect the preferred conformations in OPV and PPV systems? Moreover, one has to distinguish strictly between data measured in isotropic or in nonisotropic media. The conformational effects and their influence on absorption, fluorescence, etc. can differ significantly.



1 (n = 1, ..., 11)

One way to interpret the properties of poly(1,4-phenylenevinylene)s is to study these compounds by means of various force field[22] or quantum mechanical calculations.[24−26] A main drawback of theoretical approaches is given by starting geometries which are derived from inappropriate model compounds; *(E)*-

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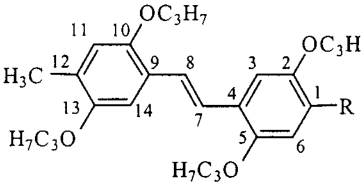
stilbene for example as a model for a substituted PPV is certainly inappropriate. The majority of the applications of PPVs and OPVs concern solids; therefore structure elucidations in the solid state are most important.

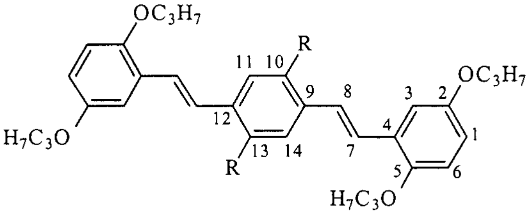
Some X-ray studies of PPV model compounds[27−32] or PPV itself[33] have been performed; however, most of the compounds represent special substitution patterns which are not applicable to the PPVs most often used in devices.

In this paper, we report the X-ray structure analyses of several model compounds (**2**−**5**) for 2,5-dialkoxy-substituted PPV and discuss the effect of substitution on the structural parameters.



2 (R = Br)

3 (R = CHO)



4 (R = H)

5 (R = OC_3H_7)

Experimental Section

The synthesis of the compounds **2**−**5** is described elsewhere.[34,35] Crystals of good quality were obtained by crystallization from methanol (compound **2**) and hexane (compounds **3** and **5**), respectively, while the crystals of the distyrylbenzene derivative **4** were obtained by slow evaporation of a chloroform solution.

X-ray diffraction measurements were performed on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Cu $K\alpha$ (l = 1.54189 Å) radiation with w/2 scans. Lattice parameters were determined by least-squares fits from at least 25 centered reflections (65° < θ < 69°). Intensities were corrected for decay of three control reflections, measured every 60 min, and for Lorentz and polarization factors but not for absorption.

The structures were solved by direct methods (SHELXS-86[36]) and refined by full-matrix least squares (SHELXL-93[37]) based on F^2. Hydrogen atoms were placed at calculated positions and refined isotropically, assuming a riding motion model. Non-hydrogen atoms were refined anisotropically. Final difference Fourier maps showed no significant features.

Results and Discussion

To study the change of the physical properties of 2,5-dialkoxy-substituted oligo(1,4-phenylenevinylene)s with growing chromophor length, we recently synthesized the homologous series **1**.[34] Now, compound **5** was selected for the crystal structure analysis and compared to the systems **2**−**4** which have different substitution patterns.

The enumeration of the atoms was chosen in a way to permit the comparison of **2**−**5**; it does not correspond to the IUPAC rules. Table 1 contains the crystallographic data of **2**−**5**; Table 2 summerizes the important structural parameters.

By comparing the bond lengths in Table 2, it is obvious, that the values for the olefinic double bonds and the adjacent single bonds are all within the expected ranges. The same statement is valid for the bond angles, which show values between 124 and 128°.

The parameters most important for conjugation are the torsion angles between the planar aromatic and olefinic moieties.[22] They differ widely over a range between 5 and 27°. However, there is no direct systematic change that could be associated with the steric interactions of the alkoxy side chains with the olefinic building blocks. This result becomes already obvious by comparing the torsion angles of the two stilbene compounds **2** and **3**, where the only difference between the molecules is the substituent in the para position C-1. Although the displacement of bromine by a formyl group should not have a noticeable influence on the torsion angle, the measured values differ by more than 7°. However, the substituents change the symmetry of the crystals from monoclinic for the bromo-substituted stilbene **2** to triclinic for the aldehyde **3**. Therefore, the crystal packing seems to be the reason for the change in the torsion angles.

When we compare the compounds **4** and **5**, the effect of different crystal symmetry cannot be taken into account since both crystals belong to the same monoclinic space group. Nevertheless, an even more pronounced difference in the torsion angles can be observed for these distyrylbenzene derivatives. The molecules **4** and **5** differ only in the substitution of the central aromatic ring. Although the substitution of the outer rings is the same, the torsion angle C3−C4−C7−C8 for compound **4** is more than twice as large as for **5**, whereas the absolute value of the torsion of the inner ring is almost the same for both compounds. This is even more astonishing, since chemical intuition would suggest that the steric repulsion between the olefinic protons and the large alkoxy substituents in the central ring of **5** is bigger compared to the effect of the small hydrogen atoms in **4**. Thus, exactly the opposite results

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Table 1. Crystallographic Data of the Compounds 2−5

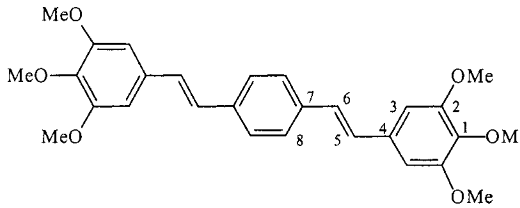
compound	**2**	**3**	**4**	**5**
formula	$C_{27}H_{37}O_4Br$	$C_{28}H_{38}O_5$	$C_{34}H_{42}O_4$	$C_{40}H_{54}O_6$
molecular weight	505.47	454.58	514.67	630.83
lattice type	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P1$	$P2_1/c$	$P2_1/c$
Cell Dimensions				
a (Å)	12.7860(2)	4.3338(3)	14.680(8)	9.3874(1)
b (Å)	4.960(1)	10.8355(4)	7.6311(4)	25.2723(4)
c (Å)	22.162(3)	14.9591(5)	16.255(3)	8.1122(3)
α (deg)	90.0	69.577(3)	90.0	90.0
β (deg)	103.100(4)	88.566(5)	126.10(2)	104.483(2)
γ (deg)	90.0	83.458(5)	90.0	90.0
V (Å^3)	1368.9(9)	653.94(6)	1471.3(9)	1863.37(9)
z	2	1	2	2
d_c (gcm^{-3})	1.226	1.154	1.162	1.124
F (000)	532.0	246.0	556.0	684.0
crystal size (mm^3)	0.10 × 0.45 × 0.06	1.10 × 0.10 × 0.06	0.07 × 0.30 × 0.35	0.10 × 0.42 × 0.10
m (mm^{-1})	2.26	0.62	0.58	0.59
Data Collection				
T (K)	298	298	295	298
θ range (deg)	2−70	2−70	1.5−70	1.5−75
data measured	3027	5599	3039	3940
unique	2226	2483	3029	3832
observed ($\|F\|/s(F) > 4.0$)	1817	2105	2098	2623
Structure Refinement				
no. variables	149	168	188	231
$R1$ (%)	5.81	5.93	4.90	7.58
w$R2$ (%)	17.79	18.25	15.39	23.95
quality of fit	1.033	1.041	1.041	0.826
max shift/s	0.000	0.000	0.001	0.001
max, min peak in final diff. Fourier map (e Å^{-3})	−0.33, 0.41, −0.39	0.21−0.25	0.14, −0.12	0.56, −0.23

Table 2. Selected Bond Lengths, Bond Angles, and Torsion Angles of the Compounds 2−5

compound	**2**	**3**	**4**	**5**
Bond Lengths (Å)				
C4−C7	1.466(4)	1.464(2)	1.477(3)	1.472(3)
C7−C8	1.323(5)	1.323(3)	1.330(3)	1.312(4)
C8−C9	1.466(4)	1.464(2)	1.468(2)	1.465(3)
Bond Angles (deg)				
C4−C7−C8	125.3(4)	126.1(2)	124.3(2)	125.5(3)
C7−C8−C9	125.3(4)	126.1(2)	127.0(2)	127.8(3)
Torsion Angles (deg)				
C3−C4−C7−C8	−18.0(6)	10.7(3)	26.5(3)	12.1(4)
C7−C8−C9−C14	+18.0(6)	−10.7(3)	6.8(3)	−5.3(5)

should be expected, namely the inner torsion angle in **5** being larger compared to that of **4**, while the outer torsion angles should be comparable. Figure 1 shows the molecular structures of **4** and **5**, particularly the view of the two distyrylbenzene molecules along the long axis, visualizing the differences in the torsion angles of both compounds.

A further comparison with the systems **6**−**9**, which are again model compounds for PPVs, confirms these results. Whereas the distyrylbenzene derivative **6**[27] can be related to compound **4** insofar as it also has an unsubstituted central benzene ring, the oligo(1,4-phenylenevinylene)s **7**,[28] **8**,[29] and **9**[30] represent more extended model compounds.



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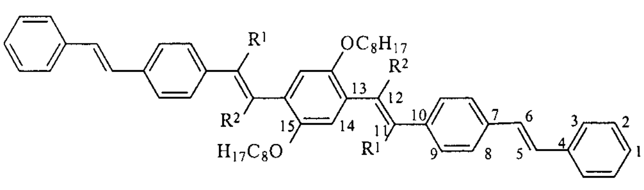

7 (R^1 = H, R^2 = H)
8 (R^1 = H, R^2 = CN)
9 (R^1 = CN, R^2 = H)

Looking at the results for these compounds, which are gathered in Table 3, it becomes obvious that again the torsion angles represent the most important data. In the OPVs **7**−**9**, the only difference is due to the presence or absence of cyano groups at the inner olefinic double bonds. While this substituent will surely influence the electronic structure as a consequence of its strong electron-withdrawing character, it should not have a pronounced influence on the geometry of the two outer, unsubstituted benzene rings and their relative orientation with respect to the outer olefinic double bonds. However, all three compounds show fairly different values for the observed torsions. Moreover, from a steric and electronic point of view, there should be no reason that the torsion angle of C3−C4−C5−C6 should be significantly different from the angle C5−C6−C7−C8; yet there are substantial deviations.

The quantum mechanically calculated[25] bond lengths for PPV and 2,5-dimethoxy-PPV for the olefinic bonds are slightly longer than the experimental values, whereas the calculated bond lengths for the adjacent single bonds are shorter than the measured values. This may be a hint that the calculated delocalization for PPV is stronger than the delocalization observed in the model compounds.

Moreover, in none of the four molecules **2**−**5** investigated in this paper can weak hydrogen bonds between the olefinic protons and the oxygen atoms of the alkoxy groups be detected. Such hydrogen bonds have been proposed by Brédas et al.[40] and Fahlman et al.[41,42] on the basis of quantum mechanical calculations for 2,2',5,5'-tetramethoxystilbene, cyano-substituted PPV, and poly(1,4-pyridylenevinylene-1,4-phenylenevinylene)s, respectively. According to these calculations, the hydrogen bonds should be responsible for a stronger planarization

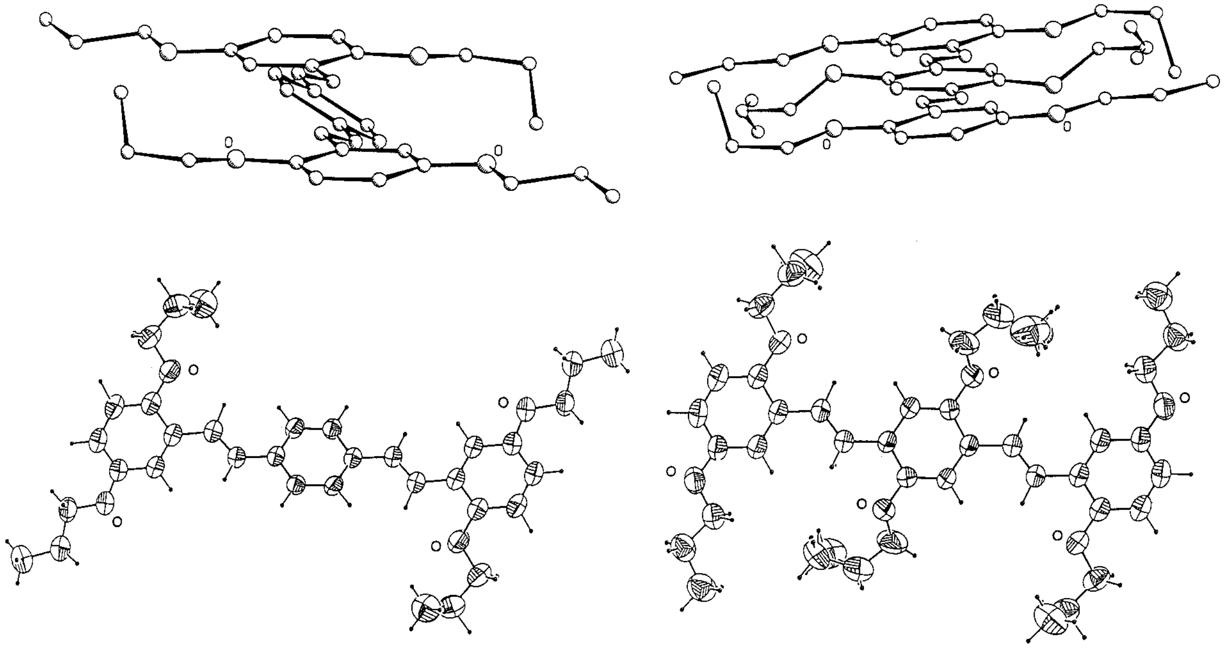

Figure 1. PLATON[38] drawing and view along the long molecular axis of **4** (left) and **5** (right).[39]

Table 3. Selected Bond Lengths, Bond Angles, and Torsion Angles of the Compounds 6−9

compound	6	7	8	9
Bond Lengths (Å)				
C4−C5	1.474	1.492/1.468	1.462	1.435
C5−C6	1.315	1.294/1.318	1.335	1.321
C6−C7	1.465	1.502/1.467	1.462	1.441
C10−C11	-	1.449/1.488	1.457	1.464
C11−C12	-	1.306/1.338	1.351	1.321
C12−C13	-	1.486/1.474	1.482	1.458
Bond Angles (deg)				
C4−C5−C6	127.4	124.1/125.4	127.2	129.6
C5−C6−C7	126.6	125.1/127.0	124.9	126.9
C10−C11−C12	-	125.1/125.3	132.4	124.9
C11−C12−C13	-	127.8/124.1	126.2	133.1
Torsion Angles (deg)				
C3−C4−C5−C6	6.8	1.5/1.0	−0.6	0.5
C5−C6−C7−C8	−5.6	6.8/4.7	−13.5	−11.2
C9−C10−C11−C12	-	14.0/9.9	−1.2	14.2
C11−C12−C13−C14	-	15.9/19.7	11.2	2.7

of the systems. However, in none of our compounds investigated by X-ray does the distance between the oxygen atom and the olefinic proton reach values below 2.4 Å. Distances above 2.4 Å are too wide to prove hydrogen bonds and should only be interpreted as being responsible for a preferential orientation of the alkoxy groups with respect to the olefinic double bonds. All compounds show an orientation of the alkoxy side chains which is perpendicular to the olefinic double bonds, just what is expected from force field calculations.[22]

Conclusion

The presented structural data for two 2,5-dialkoxy-substituted stilbenes (**2** and **3**) and two 2,5-dialkoxy-substituted distyrylbenzene derivatives (**4** and **5**) reveal no direct correlation of the torsional angles and the substitution pattern. Crystal lattice effects are the predominating factors. Weak hydrogen bonds suggested by quantum mechanical calculations[40−42] could not be verified. Moreover, such calculations seem to overestimate the conjugation effect.

As mentioned above, conformational effects in OPV and PPV compounds are important for structure−property relationships. The 2,5-disubstitution proved to be the best choice for the application of these materials in conductivity and photoconductivity experiments.[21] Alkoxy substituents reduce the HOMO−LUMO gap (band gap in the solid state). This effect increases on one hand the probability for the charge carrier formation and reduces the quantum yield for the (oxygen-free) photochemical degradation of the material; on the other hand, the torsions along the main chain can be enhanced by these substituents so that the limiting values λ_∞[23] of the absorption and the fluorescence maxima can be reduced. The present study now reveals that the torsional effect, which is valid in free or solubilized molecules, is in the crystalline state dominated by packing effects. Thus, the 2,5-disubstitution pattern seems to be especially useful for all applications in the solid state which demand small band gaps in OPVs and PPVs.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, and structure factors for compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Crystallographic data for the compounds **2**−**5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-410634-7. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK.

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