A Computational Study of 2,5-Dibenzylidenecyclopentanone and 2,6-Dibenzylidenecyclohexanone, Model Compounds for Poly(arylidenecycloalkanones)

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ABSTRACT: The relative energies of the three possible isomers of 2,5-dibenzylidenecyclopentanone and of 2,6-dibenzylidenecyclohexanone were calculated using Mechanics, MOPAC, and MOPAC with CI. The calculated lowest energy isomer of each compound agrees with known spectroscopic and crystallographic data. This work shows that the "SCF-CI" calculations previously reported on 2,5-dibenzylidenecyclopentanone do not predict the actual structure of the compound and should not be used to predict the structure of the corresponding polymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2255–2257, 1999

Key words: 2,5-dibenzylidenecyclopentanone; 2,6-dibenzylidenecyclohexanone; arylidenecycloalkanone; poly(arylidenecycloalkanones); computation

INTRODUCTION

In the course of investigating the chemistry of a polymer of 1,3-arylidene-2-indanones, we reviewed the synthesis of the conjugated polymers of arylidenecycloalkanones, namely poly(2,5-arylidenecyclopentanone) and poly(2,6-arylidenecyclohexanone), obtained by condensation of cyclopentanone or cyclohexanone with terephthalaldehyde using catalytic amounts of alcoholic potassium hydroxide.[1] The model compounds for these polymers, 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone, were of particular interest to us. The condensation of either cyclopentanone or cyclohexanone with benzaldehyde cleanly gives only one of the three possible isomers shown in Figure 1. We were interested in whether the condensation of 2-indanone with benzaldehyde would similarly give one isomer, and if this chemistry could be used to prepare poly(1,3-arylidene-2-indanones), which would be fully conjugated instead of crossconjugated as are poly(2,5-arylidenecyclopentanone) and poly(2,6-arylidenecyclohexanone).

Our preparation of 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone confirmed the fact that one isomer is produced. The ^{1}H- and ^{13}C-NMR spectra of the compounds were consistent with the spectra in the literature, and clearly show the products are symmetrical.[2,3] Crystal structures of both compounds show the arrangement of the phenyl rings is towards the ring of the cycloalkane core as in **1** and **4** (the (*E*, *E*) isomer).[4,5] Abd-Alla and coworkers have reported using "SCF-CI" (Self Consistent Field-Configuration Interaction) calculations that "from the π-electron energy of the ground state, the *trans* form [**2**] is lower than the *cis* form [**1**] by 91.029 kcal/mol; hence, this model compound has the *trans* form [**2**]."[3] From the NMR data of these authors and others, this is clearly not the case, and this is confirmed by the existing crystal structures. The magnitude of the difference in energy between the two isomers reported by these au-
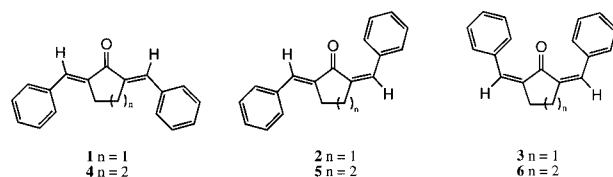
Figure 1 (E, E), (E, Z), and (Z, Z) isomers of 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone.

thors is much larger than typical energy differences between such isomers. We have completed calculations that accurately predict the lowest energy isomer of both 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone are **1** and **4**, respectively (the (E, E) isomer). The "SCF-CI" calculations used by Abd-Alla et al. predicts the incorrect order of stability as well as an unreasonable energy difference between compounds **1** and **2**. The "SCF-CI" calculations and results cannot be used as presented to predict the order of stability of the compounds or the structure of the corresponding polymer.

EXPERIMENTAL

Preparation of 2,5-Dibenzylidenecyclopentanone and 2,6-Dibenzylidenecyclohexanone

2,5-Dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone are both available commercially. The compounds were prepared according to the literature.[6]

Calculations

All calculations were completed with the calculational chemistry software package CAChe (Computer Aided Chemistry) (Release 3.9) from CAChe Scientific, Inc. Three levels of calculation—mechanics, molecular orbital package (MOPAC), and MOPAC with configuration interaction (CI)—were used. A typical calculation was run in the following manner: a structure was drawn with CAChe editor and adjusted to the desired starting geometry. The structure was then optimized using CAChe mechanics (augmented MM2 parameters). The resulting structure was optimized with MOPAC (PM3 parameters). The structure was further minimized incorporating configuration interaction (CI = 4). The sequence of calculations was run from a variety of starting geometries,

including the crystallographic structure, to assure that the global minimum was found.

RESULTS AND DISCUSSION

Abd-Alla et al. have reported extensively on the synthesis of arylidene polymers.[1,3,7–9] In our own work on highly conjugated polymers, we became interested in 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone as model compounds for a 1,3-arylidene-2-indanone. Abd-Alla has reported molecular orbital studies on arylidenecycloalkanones as models for polymers and copolymers of arylidenecycloalkanones.[3,9] We were at once curious about these reports because there are actually three possible isomers **1–3**, shown in Figure 1 that could be produced from the condensation of cyclopentanone with benzaldehyde, and only two structures, **1** and **2**, were considered in the reported calculations.[3] Furthermore, the reported ¹H-NMR data of these compounds in the article was inconsistent with the unsymmetrical structure predicted from the author's calculations. The spectra, however, are consistent with other spectra in the literature for these compounds. To investigate these inconsistencies further, we made both 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone. The reactions each cleanly give one product with the same ¹H-NMR data reported by Abd-Alla.[3] Interpretation of these spectra leads one to believe that either of the symmetrical isomers is the more probable structure due to the simplicity of the spectra. The ¹³C-NMR spectra of 2,5-dibenzylidenecyclopentanone contains eight distinct resonances, and that of 2,6-dibenzylidenecyclohexanone contains nine, again suggesting one of the symmetrical isomers **1** and **4** or **3** and **6**. A literature search revealed that crystal structures of both compounds had previously been reported, and the symmetrical compounds **1** and **4** are the correct structures.[4,5]

Calculations were then performed to investigate whether the correct lowest energy structure can be predicted. Our calculations did not lead to the same results as obtained by Abd-Alla, but instead, correctly predicted at three different levels of theory that **1** and **4** would be the most stable isomers of 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone, respectively. A summary of these calculations is presented in Table I. In the case of 2,5-dibenzylidenecyclopentanone, the trend in energy is **1** < **2** < **3** at each

Table I Summary of Computational Results

Structure	Mechanics[a]	MOPAC[a]	MOPAC CI[a]
1	−2.987	35.983	33.958
2	−0.871	39.258	38.096
3	0.183	42.598	*[b]
4	−4.964	35.263	33.881
5	−3.220	37.694	36.462
6	−4.011	36.612	35.350
7	−9.347	77.625	74.779
8	−9.967	78.851	76.590
9	−10.877	80.212	*[b]

[a] kcal/mol
[b] *degenerate energy levels detected

level of theory. In the case of 2,6-dibenzylidene-cyclohexanone the trend is **4** < **6** < **5**. The lowest energy structures calculated for **1** and **4** are not planar. In **1**, the phenyl rings are tilted 35° out of plane relative to the five-membered ring, which is virtually flat. In **4**, the phenyl rings are tilted 57–58° out of plane relative to the adjacent pi-system, and the cyclohexanone is in a half-chair–like conformation. The crystallographic data show the structure of **1** is almost flat with the phenyl rings 3° out of plane relative to the five-membered ring. The crystal structure of **4** is not flat with one phenyl ring 29° and the other 40° out of plane relative to the adjacent pi-system; the cyclohexanone is in a half-chair conformation. The difference in planarity between the isolated molecule calculation and the crystal structure determination is likely due to the packing forces that are present within the crystal.

In our investigation of the feasibility of preparing poly(1,3-arylidene-2-indanones) we used the condensation of 2-indanone with benzaldehyde to prepare 1,3-arylidene-2-indanone as a model reaction. Using MOPAC and MOPAC with CI the (*E*, *E*) isomer **7** was predicted to be more stable than the (*E*, *Z*) **8** and the (*Z*, *Z*) **9** isomers; however, at the mechanics level the opposite trend was observed as shown in Table I. The reaction did give **7** as the major product with trace amounts of **8** and **9** present. The overall yield of **7**, however, was extremely low, approximately 18%, and the reaction as a whole was deemed unsuitable for the intended preparation of poly(1,3-arylidene-2-indanones).

CONCLUSIONS

The base-catalyzed condensation of cyclopentanone or cyclohexanone with benzaldehyde gives 2,5-dibenzylidenecyclopentanone and 2,6-dibenzylidenecyclohexanone as the **1** and **4** isomers, respectively. Existing spectroscopic and crystallographic data in the literature confirm these structures. Conventional computational chemistry can be used to accurately predict the lowest energy product of the condensation, contrary to the results of Abd-Alla et al. The "SCF-CI" calculated energy differences reported by Abd-Alla et al. for **1** and **2**[3] and other model compounds for poly(arylidenecycloalkanones) not mentioned in this article[9] are extraordinarily large, and are not reasonable energy differences between the compounds, and, therefore, cannot be used to predict relative energies of the compounds or to predict the structure of the corresponding polymers.

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