



## Binary amorphous solids consisting of 2,4,6-triarylphenoxy radicals and their dimers



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### ARTICLE INFO

#### Article history:

Received 28 March 2017

Revised 10 May 2017

Accepted 12 May 2017

Available online 13 May 2017

#### Keywords:

Binary amorphous

Phenoxy

Monomer-dimer equilibrium

Chemical exchanges in solid state

### ABSTRACT

Although molecular amorphous materials represent an important area of research in solid-state chemistry, studies pertaining to these systems have been restricted almost exclusively to amorphous solids based on a single molecule. In this study, we found that, while the 2,4,6-bis(4-*tert*-butylphenyl)phenoxy radical (**2<sub>M</sub>**) and its dimer (**2<sub>D</sub>**) did not give single-component amorphous solids, they rapidly formed the corresponding binary amorphous solid **IIa** following their condensation from benzene, dichloromethane, chloroform, and ethyl acetate solutions. The formation of **IIa** could be attributed to the good solubilities of **2<sub>M</sub>** and **2<sub>D</sub>** in these solvents and the high packing efficiencies of these amorphous solids. **IIa** was also obtained when crystals of **2<sub>D</sub>** (**IIb**) were ground together. The solid-state formation of **IIa** would not only involve the locational exchange of **2<sub>M</sub>** and **2<sub>D</sub>**, but would also involve chemical exchanges.

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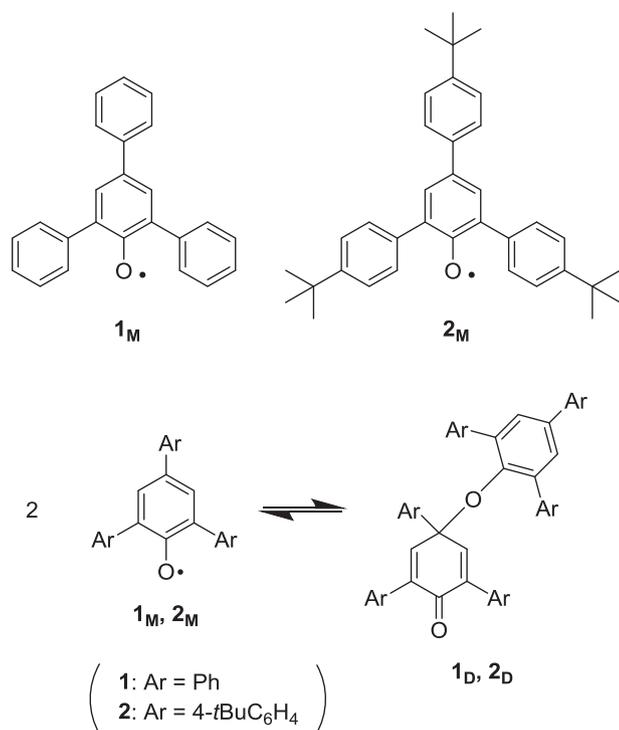
Multicomponent (binary, ternary, and increasingly complex systems) crystals represent diverse materials for research towards solid-state chemistry and physics because they can impart various functional characteristics, which can be used to tune the properties of other components.<sup>1</sup> Moreover, numerous research opportunities still exist to expand upon our collective understanding of this area with new features. These advantages are also promising for the development of multicomponent amorphous solids,<sup>2</sup> which exhibit no long-range order between their individual components. Based on their unique structural features, amorphous solids composed of alloys, metal oxides, and polymers have been used extensively as structural, magnetic, and electronic materials. Molecular amorphous materials have also been extensively studied. Amorphous drugs have several advantages over the corresponding crystalline materials in terms of their high stability and solubility.<sup>3</sup> Furthermore, given that exciton decay processes can be avoided using amorphous solids, amorphous thin films can be used as charge transport layers in organic light-emitting diodes.<sup>4</sup> Although a large number of these amorphous solids exist as multicomponent systems, their amorphous characteristics originate from a single host component, with the other guest components simply behaving as

passengers without disturbing the amorphous characteristics of the host lattice. In some cases, although the individual components of a mixture can crystallize under general conditions, as a mixture they can readily form amorphous solids. For example, ether-isopentane-alcohol, 3-methylpentane-isopentane, and ethanol-methanol mixtures are frequently used to prepare frozen solutions, which exist as amorphous solids. These amorphous solids can be referred to as *true multicomponent amorphous solids*.

To further diversify the field of solid-state chemistry, it is important to develop new true multicomponent amorphous solids. Despite the need for further development in this area, studies pertaining to new true multicomponent amorphous solids are rare. In this study, we have investigated the preparation of true binary amorphous solids consisting of 2,4,6-triarylphenoxy radicals (**1<sub>M</sub>** and **2<sub>M</sub>**) and their dimers (**1<sub>D</sub>** and **2<sub>D</sub>**).<sup>5</sup> 2,4,6-Triarylphenoxy radicals generally exist in a monomer-dimer equilibrium in solution.<sup>6</sup> In contrast, however, 2,4,6-tri-*tert*-butylphenoxy radicals exist almost exclusively as monomeric radicals in the solid and solution state because of the bulky substituents at their 4-positions.<sup>7</sup> The condensation of solutions of almost all of the known 2,4,6-triarylphenoxy radicals results in the formation of crystals of the corresponding dimeric species. This is also the case for 2,4,6-triphenylphenoxy radicals (**1<sub>M</sub>**), which exists in a monomer-dimer (**1<sub>M</sub>**/**1<sub>D</sub>**) equilibrium in solution, as depicted in [Scheme 1](#). Furthermore, the condensation of solutions of **1<sub>M</sub>** and

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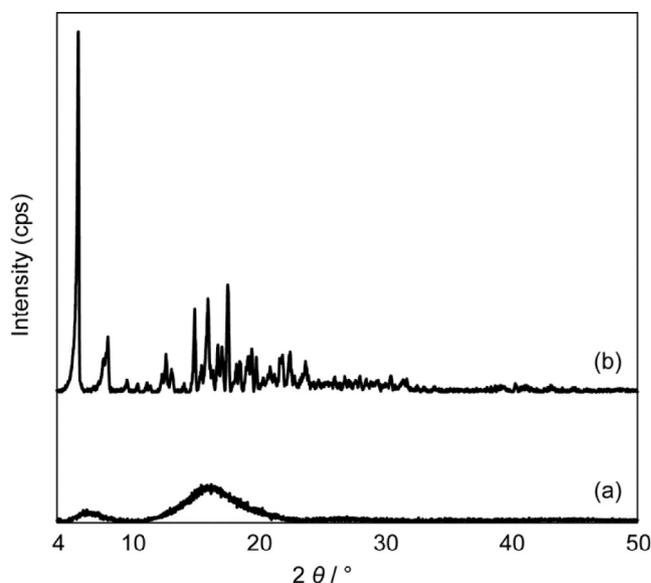


**Scheme 1.** Monomer–dimer equilibria of **1M/1D** and **2M/2D**.

**1D** leads to the formation of dimer crystals (**1b**),<sup>8</sup> irrespective of the solvent used. In contrast, the solidification behavior of 2,4,6-tris(4-*tert*-butylphenyl)phenoxy radicals (**2M**) was different to that of **1M**.<sup>9</sup> While hexane solutions of **2M** and **2D** gave dimeric crystals of **1b**, benzene solution of these materials gave the purple glassy solid **1a**. Dimroth and co-workers referred to **1a** as a “glasartige Rückstand” (glassy residue),<sup>10</sup> the purple color of which was attributed to the presence of **2M**. There have, however, been no further reports describing **1a** in the literature.

Phenoxy radical **2M** was prepared by the oxidation of the corresponding phenol with  $\text{K}_3[\text{Fe}(\text{CN})_6]$  under basic conditions (See [Electronic Supplementary Information](#)).<sup>8</sup> The condensation of the resulting purple solution consisting of **2M** and **2D** afforded the deep purple solid **1a**. The analysis of this solid by X-ray powder diffraction (XRD) revealed no diffraction peak, which indicated that **1a** was an amorphous solid (Fig. 1). It is noteworthy that the treatment of 2,4,6-triphenylphenol (precursor of **1M**) under the same conditions gave virtually colorless crystals of **1b** consisting exclusively of **1D** (Fig. 2(a)). The condensation of a dichloromethane, chloroform, or ethyl acetate solution of **2M** and **2D** afforded only **1a**. In contrast, the condensation of a hexane or acetone solution of **2M** and **2D** resulted in the formation of virtually colorless crystals of **1b** consisting of **2D**, which was confirmed by single-crystal X-ray analysis (Fig. 2(b)).

We initially considered the possibility that **1a** consisted entirely of **2M** because these crystals were the same color as a benzene solution of **2M**, and numerous compounds bearing pseudo  $\text{C}_3$ -symmetric molecular structures have been reported to give amorphous solids.<sup>11</sup> However, the infrared (IR) spectrum of **1a** was similar to that of **1b** (Fig. S1), indicating that the main component of **1a** was **2D**. A comparison of the IR spectra of **1a** and **1b** revealed several differences. As shown in [Fig. 3](#) (top), the IR spectra of **1a** and **1b** contained peaks around  $1600\text{ cm}^{-1}$ , which nearly merged in **1a** but were well separated in **1b**. Notably, the IR spectrum of **1a** contained peaks at  $1564$  and  $1556\text{ cm}^{-1}$ , which did not appear in **1b**. Given that the color of **1a** was indicative of the presence of



**Fig. 1.** XRD charts ( $\lambda_{\text{Cu}, \text{K}\alpha} = 1.5418\text{ \AA}$ ) of **1a** (a) and **1b** (b).

**2M**, the IR absorption peaks of **2M** and **2D** were simulated using (U)B3LYP/6-31G(d,p) calculations and compared with the observed IR spectra. As shown in [Fig. 3](#) (bottom), the simulation accurately reproduced the observed spectra of **1b**. Furthermore, the differences between **1a** and **1b** were in good agreement with the simulated peaks of **2M**, indicating that **2M** was indeed present in **1a**. Given that all of the peaks observed in the IR spectrum of **1a** were assigned to **2D** and **2M**, **1a** was confirmed to consist entirely of these molecules.

The molar ratio of **2M** to **2D** in **1a** was estimated based on electron paramagnetic resonance (EPR) measurements. Before measuring the EPR spectra of **1a**, we confirmed that the EPR signal intensity (integration values) was proportional to the spin number irrespective of the molecular structure using several standard radical compounds. The calibration line obtained in this way was used to evaluate the EPR signal intensity of the weighted amount of **1a**, and the content of **2M** in **1a** was estimated to be about 9% (See [Electronic Supplementary Information and Fig. S2](#)). The observed density of **1a** ( $1.029\text{--}1.033\text{ g cm}^{-3}$ ) was used to determine the  $[\text{2D}]/[\text{2M}]^2$  value of **1a**, which was found to be  $8.8 \times 10^{-3}\text{ (M}^{-1}\text{)}$ . Notably, the molar ratio of **2M** to **2D** in **1a** was different to the value found in a benzene solution. The dimerization constant  $K (= [\text{2D}]/[\text{2M}]^2)$  in a dilute benzene solution of **2M** and **2D** was determined to be  $4.5 \times 10^{-5}\text{ (M}^{-1}\text{)}$ ,<sup>12</sup> which differed considerably from the  $[\text{2D}]/[\text{2M}]^2$  value in **1a**. This result therefore indicated that **1a** could not be regarded as a static structural representation of the **2M/2D** equilibrium in a saturated benzene solution. At this stage we began to wonder why a mixture of **2M** and **2D** readily formed the true binary amorphous solid **1a**, whereas mixtures of **1M** and **1D**, and several other related compounds did not show similar properties. This difference in the behaviors of these materials could be attributed in part to the enhanced solubility of **2M** and **2D** in benzene and the other non-polar solvents mentioned above because of their *tert*-butyl substituents. These groups would lead to the rapid solidification of solutions of **2M** and **2D** under highly concentrated conditions. Notably, these conditions would provide a kinetic advantageous for the preparation of amorphous solids. This hypothesis was supported by the fact that hexane and acetone solutions of **2M** and **2D**, which were both less soluble in these solvents than they were in benzene, produced **1b**.

Another reason for the facile formation of **1a** is that these amorphous solids are thermodynamically stable. The chemistry of

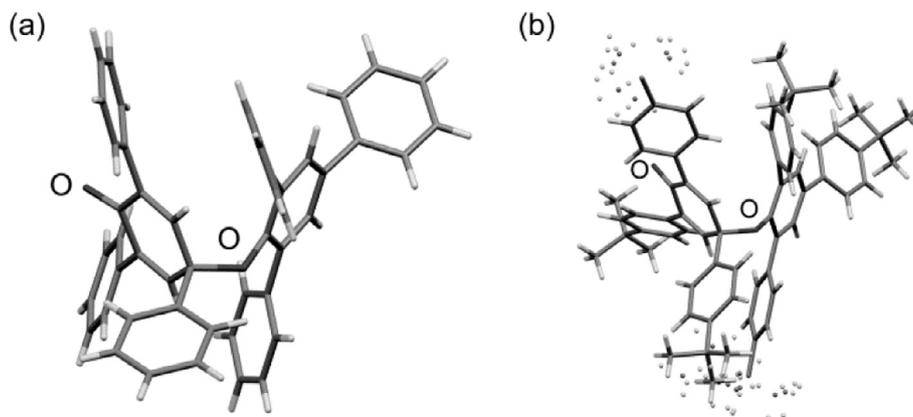


Fig. 2. X-ray structures of **Ib** (a) and **IIb** (b). Two of the *tert*-butyl groups of **2<sub>D</sub>** were disordered in **IIb**. Oxygen atoms are designated.

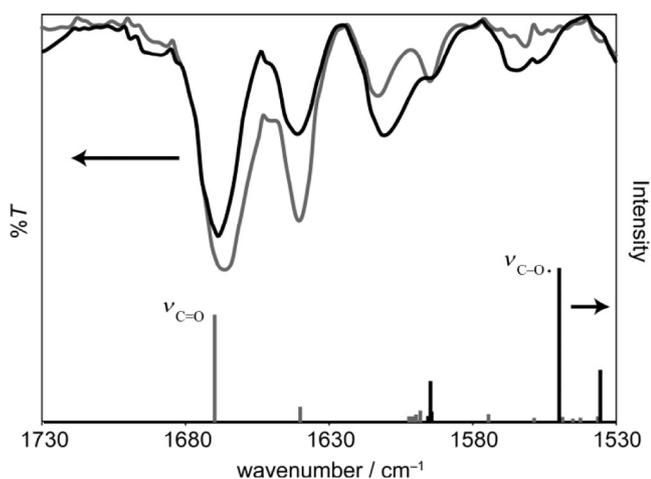
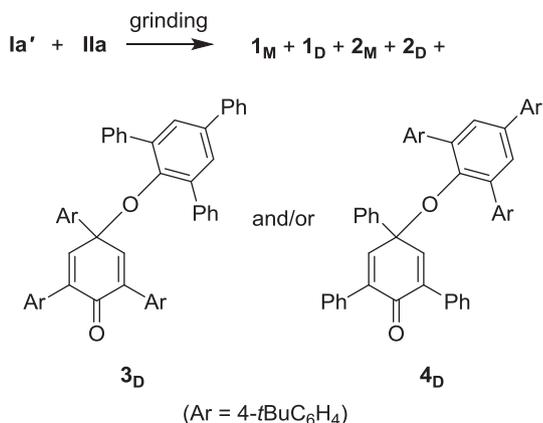


Fig. 3. (top) IR spectra (zoom) of **IIa** (black curve) and **IIb** (gray curve). (bottom) Simulated IR absorption peaks of **2<sub>M</sub>** (black bars) and **2<sub>D</sub>** (gray bars) obtained by (U)B3LYP/6–31 G(d,p) calculations, where  $\nu_{\text{C=O}}$  and  $\nu_{\text{C-O}}$  appear at 1670 and 1550  $\text{cm}^{-1}$ , respectively.

crystalline materials clearly shows that closely packed structures are energetically favored over loosely packed lattices, as indicated by the principle of close packing.<sup>13</sup> This principle can be extended to non-crystalline solids because the packing efficiency of amorphous solids, which are thermodynamically less stable than crystalline materials, is lower than that of crystals of the same composition in almost all cases. Moreover, a comparison of binary systems consisting of the same components but with different component ratios revealed that the more closely packed amorphous solids were the most stable materials.<sup>14</sup> Although no general tendency has been observed in the packing efficiency of amorphous solids compared with their corresponding crystal forms, their amorphous areas are known to be less densely packed by up to 10% compared with the corresponding crystalline areas in polymers.<sup>15</sup> If this was applicable to molecular amorphous materials, then the packing efficiency of **IIa** (0.711–0.713) would have to be considered as unexpectedly high given that it is only a little bit smaller than that of **IIb** (0.724–0.725). Considering the principle of close packing, this result therefore indicates that amorphous **IIa** was being stabilized in a thermodynamic manner.<sup>16</sup> The facile formation of **IIa** was reminiscent of amorphous alloys<sup>17</sup> and metal glasses,<sup>18</sup> which are also densely packed amorphous solids consisting of two or three atoms of different sizes. Although it still remains unclear why mixtures of **2<sub>M</sub>** and **2<sub>D</sub>** form closely packed

solids, they could be behaving in a similar manner to metal glasses,<sup>19</sup> with the smaller molecules (**2<sub>M</sub>**) simply filling the voids between the larger molecules (**2<sub>D</sub>**) in an effective manner.

When **IIb** was vigorously ground in a pestle and mortar, it immediately became red in color and ultimately formed a deep purple solid after 90 min.<sup>20</sup> The resulting solid **IIa'** gave a similar IR spectrum and XRD pattern to those of **IIa**, although the XRD pattern did still show the Bragg diffraction peaks of **IIb** (which failed to disappear even after several hours of grinding). Moreover, the concentration of an acetone solution of **IIa'** led to the quantitative formation of **IIb**. Accordingly, **IIa'** should mainly consist of **IIa** with a small amount of **IIb**. Unfortunately, it was not possible to determine the yield of **IIa** because of the presence of unreacted **IIb**. These results may therefore indicate that the thermodynamic stabilities of **IIa** and **IIb** were similar.<sup>21</sup> As reported previously, **Ib** became red in color when it was ground in a pestle and mortar.<sup>8</sup> The resulting solid **Ia'** was subjected to IR, ESR, and XRD analyses, which revealed that it consisted of a mixture of unreacted **Ib** and amorphous **Ia**. Furthermore, the amorphous **Ia** should consist of **1<sub>D</sub>** with a small amount of **1<sub>M</sub>**, as seen in **IIa**. The generation of **Ia** therefore indicated that this material may be as thermodynamically stable as **Ib** in a similar manner to **IIa** versus **IIb**. However, the concentration of mixed solutions of **1<sub>M</sub>** and **1<sub>D</sub>** failed to afford any **Ia**, most likely because of the lower solubility of **1<sub>M</sub>** and **1<sub>D</sub>**, which would prevent the rapid solidification of these materials to give an amorphous solid. The generation of **IIa** from **IIb** by grinding could be initiated by the dissociation of **2<sub>D</sub>** to give **2<sub>M</sub>** under mechanical agitation. In fact, similar radical dissociations have been reported for the grinding of dimeric molecules in the solid state, although the products of these reactions are generally crystalline in nature.<sup>22</sup> Consequently, the molecules would be arranged without any long-range order to give amorphous solids. The molecular arrangement would therefore not only involve locational exchange (i.e.,  $\text{M}^{(1)} - \text{M}^{(2)} + \text{M}^{(3)} \rightarrow \text{M}^{(3)} + \text{M}^{(1)} - \text{M}^{(2)}$ , where M and M–M represent the monomer and dimer molecules, respectively), but would also involve chemical exchange (i.e.,  $\text{M}^{(1)} - \text{M}^{(2)} + \text{M}^{(3)} \rightarrow \text{M}^{(1)} + \text{M}^{(2)} - \text{M}^{(3)}$ ). The occurrence of the latter of these two processes was strongly supported by the mass spectrum of a ground mixture of **Ia'** and **IIa**, which not only showed molecular ion peaks corresponding to **1<sub>D</sub>** and **2<sub>D</sub>** but also contained peaks corresponding to the cross dimers **3<sub>D</sub>** and/or **4<sub>D</sub>** (Scheme 2).<sup>23</sup> The occurrence of a chemical exchange process between the two components would disrupt the elimination of the other component (**2<sub>M</sub>**) and the appropriate rearrangement of the **2<sub>D</sub>** molecules during the normal crystallization process. This could explain why the grinding of **IIb** and **Ib** afforded poorly ordered solids (i.e., amorphous solids).



**Scheme 2.** Generation of cross dimer  $\text{3}_D$  and/or  $\text{4}_D$  by mixed grinding of  $\text{Ia}'$  and  $\text{IIa}$ .

In conclusion, this paper describes the formation of the true binary amorphous solids  $\text{IIa}$  consisting of triarylphenoxyl radicals ( $\text{2}_M$ ) and the corresponding dimer ( $\text{2}_D$ ). In contrast to other 2,4,6-triarylphenoxyl systems,  $\text{2}_M$  and  $\text{2}_D$  readily formed the amorphous solid  $\text{IIa}$  when they were condensed from benzene solutions consisting of  $\text{2}_D$  with ca. 9% of  $\text{2}_M$ . The facile formation of  $\text{IIa}$  could be attributed to several factors, including the good solubility of  $\text{2}_M$  and  $\text{2}_D$  in benzene (resulting from the *tert*-butyl substituents), which led to the rapid solidification of the substrate compared with several other solvents (e.g., hexane), and the closely packed structure of  $\text{IIa}$ . Chemical exchange between  $\text{2}_M$  and  $\text{2}_D$  could also be involved in this process, playing an important role in the conversion of  $\text{IIb}$  to  $\text{IIa}$  by solid-state grinding. Further research towards understanding the solidification behavior of related compounds is currently underway in our laboratory, together with research aimed at elucidating the mechanisms responsible for the formation of amorphous solids.

### A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2017.05.040>.

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