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Crystal engineering in the aminophenols. Novel carborundum network in a supramolecular homologous series

Archan Dey,[a] Gautam R. Desiraju,*[a] Raju Mondal[b] and Judith A. K. Howard*[b]
[a] *School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.*
E-mail: desiraju@uohyd.ernet.in
[b] *Department of Chemistry, University of Durham, Durham, UK DH1 3LE*

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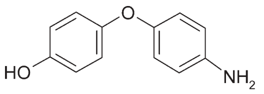
Molecular complexes of 4-(4-aminophenoxy)aniline with a series of diphenols are structurally homologous and adopt the carborundum III topology, which is an unprecedented network for organic solids.

A key concern in crystal engineering is the ability to predict the packing of new molecular solids from known crystal structures.[1] We have investigated some 20 aminophenols with respect to the relationships between molecular structure and packing type.[2] Principally, we found that when the C–O and C–N vectors are nearly parallel in the molecular structure (as in the archetypal 4-aminophenol), there is a saturation of N–H···O and O–H···N hydrogen bonds leading to the formation of tetrahedral sheets constituted with hexagons of these hydrogen bonds. This is referred to as the β-As network.[3] The phenyl rings connect the β-As sheets to complete the structure. When the C–O and C–N vectors are not parallel, we observed that more complex structures are obtained, with unsaturated hydrogen bond patterns and weak N–H···π bridges. However, we also noted that aminophenol **1** is unusual in that while it is a bent molecule (C–O to C–N angle, 140°), it still forms a β-As structure. Among other reasons, this unusual packing was ascribed to the presence of supporting C–H···O hydrogen bonds.



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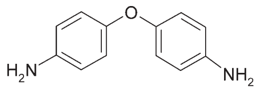

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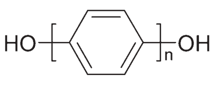

3a, n = 1 **4a = 2•3a**
3b, n = 2 **4b = 2•3b**
3c, n = 3 **4c = 2•3c**

This paper describes molecular complexes formed by the related dianiline, **2**. Dianilines and diphenols form stoichiometric binary complexes, the crystal structures of which are governed by the principles of amine–hydroxy recognition.[3,4] For example, hydroquinone and *p*-phenylenediamine give a 1 : 1 molecular complex that has a β-As structure like 4-aminophenol. Likewise, 4,4′-dihydroxybiphenyl and 4,4′-diaminobiphenyl form a 1 : 1 solid that mimics 4-hydroxy-4′-aminobiphenyl. Noting further that **1** has an unusual crystal structure, we co-crystallized **2** with **3a–c**. In each case we obtained the respective 1 : 1 adducts, **4a–c** (Fig. 1) and the following important points emerge.

(a) Aminophenol crystal structures may be predicted. In each case (**4a–c**), the β-As sheet structure is formed†. The general guideline is that any aminophenol HO–Ar–NH_2 that gives the β-As sheet structure may be expanded into a dianiline H_2N–Ar–NH_2 and a diphenol HO–Ar′–OH. The dianiline and the diphenol will then form a 1 : 1 molecular complex, which will also have the β-As sheet structure. Ermer and Eling showed this for the simpler aminophenols wherein the C–O and C–N vectors are nearly parallel.[3] The present result is impressive in that such modular behaviour is also observed in a non-linear aminophenol like **1**. As in **1**, the β-As structure in **4a**, **4b** and **4c** is stabilized by C–H···O bonds within the dianiline component (2.50 Å, 135°). The hydrocarbon regions act as spacers between the β-As sheets, and it matters little whether the ends of the molecules have two –OH groups, two –NH_2 groups or one –OH and one –NH_2 group. The hydrogen bonded and hydrophobic regions of these β-As structures are structurally well insulated (isolated) from each other. Insulation is always a valuable attribute and can thus lead to modular strategies for crystal engineering.

(b) Aminophenols show structural homology. There are surprisingly few well documented examples of supramolecular homology in molecular solids. Benzene, biphenyl and *p*-terphenyl form one such homologous series[5] and likewise so do structures **4a**, **4b** and **4c**. All three crystal structures are obtained in space group *Pbcn*, with the diphenol component lying on a $\bar{1}$ and the dianiline on a 2-axis. The *a* and *b* axial values are nearly the same in the three cases with the *c*-axis increasing from 35.145 Å to 43.441 Å to 51.733 Å, corresponding to the phenylene spacers. Such behaviour is unusual. A CSD search of compounds that form molecular complexes with both diphenols **3a** and **3b** (adducts of diphenol **3c** have not been reported in the structural literature before this study) revealed five such pairs of molecular complexes. In three of these pairs (COHWIF/NISLOQ, FOQHEY/FOQHOI, GUSSES/GUSRER) there is no structural homology. Surprisingly, the two pairs that do show homology (PITYAS/PITYIA, PITYEW/PITYOG) are from the aminophenol family and have the β-As sheet structure! Supramolecular homology clearly follows then from structural insulation. Only if the hydrocarbon and hydrogen bonded regions in these crystals were well insulated, would such phenyl → biphenyl → terphenyl homology be possible. Effectively,

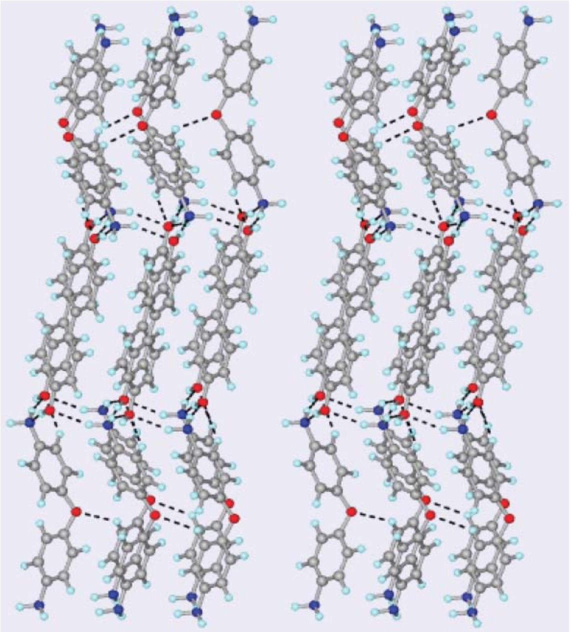

Fig. 1 Stereoview of the crystal structure of **4b**. Notice the diamine and diphenol components, and the β-As sheets of N–H···O and O–H···N hydrogen bonds. The C–H···O interactions are also indicated. The structures of **4a** and **4c** are constructed similarly with only the dimensions of the hydrocarbon spacers of the diphenol component being different.

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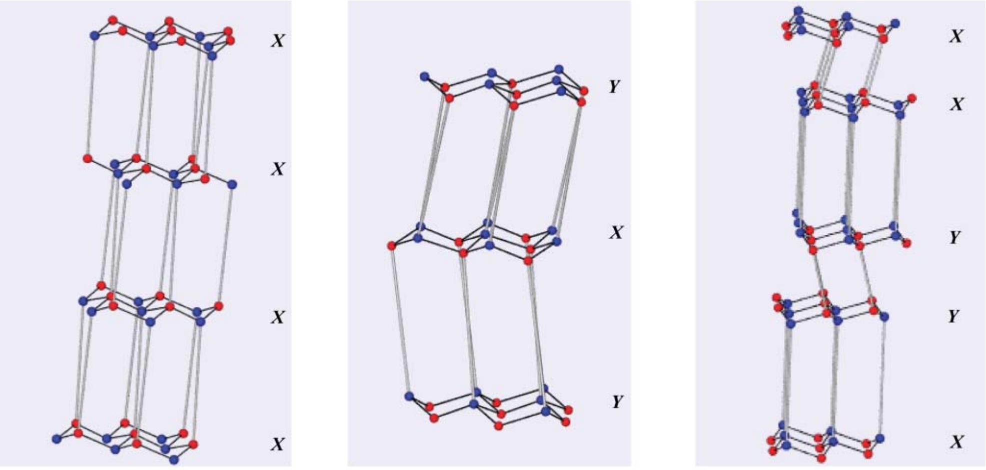

(a) (b) (c)

Fig. 2 Network depictions of (a) aminophenol **1**, zinc blende; (b) 4-hydroxy-4′-aminobiphenyl, wurtzite; (c) molecular complex **4a**, carborundum III. Hydrogen bonds are shown as dark lines and the molecular connections are shown in grey. Notice the *X* and *Y* designations of the hydrogen bonded β-As sheets.

the hydrocarbon regions of these crystalline aminophenols approximate to the crystal structures of the pure hydrocarbons themselves. Since benzene, biphenyl and *p*-terphenyl form a structural homologous series,[5] the same follows for compounds **4a**, **4b** and **4c**.

(c) Aminophenols show novel network structures. The spatial relationships between the β-As sheets define the network possibilities for these structures. Network depictions of aminophenol **1**, 4-hydroxy-4′-aminobiphenyl and complex **4a** are given in Fig. 2. The hexagonal nets are designated *X* and *Y* based on the conformational preference of the 'supramolecular chair cyclohexane'[8] of hydrogen bonds. The zinc blende (cubic ZnS) network is obtained when *X* sheets are arranged in an offset manner (Fig. 2a). The wurtzite (hexagonal ZnS) network is seen when *X* and *Y* sheets alternate in an eclipsed manner (Fig. 2b) and is far less common.[6] However, in **4a**, **4b** and **4c** there is an alternation of two *X* sheets and two *Y* sheets so that there are elements of both zinc blende and wurtzite topologies within the same structure. Such a network is unprecedented in molecular solids and corresponds to the carborundum III polytype of SiC.[7] Tetrahedral networks of organic compounds and coordination polymers are based either on zinc blende or wurtzite but not both; network polymorphism is unknown.[9] Indeed, there is no example where both these domains are found within the same network as in the present case. A rationalization for the occurrence of this unusual carborundum network in **4a**, **4b** and **4c** follows from an adaptation of the argument of Ermer and Eling.[3] The zinc blende network is centrosymmetric while the wurtzite network is not. In our molecular complexes, the diphenol components have inversion symmetry while the dianiline does not. Accordingly, the β-As sheets on either side of the diphenol molecules have the zinc blende topology while those that flank the dianiline molecules have the wurtzite topology. Such chirality or symmetry control of a network may have future potential in crystal engineering strategies, even as we are aware that such a 'rule' is not infallible in the aminophenols. For example, compound **1** which does not have $\bar{1}$ symmetry, still adopts the zinc blende network.

It is entirely possible that other carborundum polytypes[7] will be found in this family of molecular solids in the future. In conclusion, the aminophenols afford valuable entry points into the crystal engineering of molecular solids, based upon synthetic strategy, structural homology and network properties.

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Notes and references

† Data were collected using a Bruker SMART 1K-CCD area detector. *Crystal data* for **4a**: solvent of crystallization 1 : 1 CH_3CN/PhMe, mp 191.14 °C: $(C_6H_6O_2)\cdot(C_{12}H_{12}N_2O)$, $M = 310.34$, orthorhombic, $a = 5.4523(2)$, $b = 7.9556(2)$, $c = 35.1453(11)$ Å, $V = 1524.47(8)$ Å^3, $T = 120(2)$ K, space group *Pbcn*, $Z' = 0.5$, $\mu(\text{Mo-K}\alpha) = 0.093$ mm^{-1}, size $0.38 \times 0.28 \times 0.10$ mm^3. 12094 total reflections of which 1754 were independent, 1480 observed $[I > 2\sigma(I)]$. Refinement against *F*2 with 141 parameters, $R1\ [I > 2\sigma(I)] = 0.0387$.

Crystal data for **4b**: solvent of crystallization 1 : 1 : 1 EtOAc/MeCN/EtOH, mp 228.12 °C: $(C_{12}H_{10}O_2)\cdot(C_{12}H_{12}N_2O)$, $M = 386.44$, orthorhombic, $a = 5.4647(1)$, $b = 7.9338(2)$, $c = 43.4412(10)$ Å, $V = 1883.43(7)$ Å^3, $T = 120(2)$ K, space group *Pbcn*, $Z' = 0.5$, $\mu(\text{Mo-K}\alpha) = 0.091$ mm^{-1}, size $0.40 \times 0.38 \times 0.10$ mm^3. 15236 total reflections of which 2165 were independent, 1801 observed $[I > 2\sigma(I)]$. Refinement against *F*2 with 176 parameters, $R1\ [I > 2\sigma(I)] = 0.0417$.

Crystal data for **4c**: solvent of crystallization 1 : 1 EtOH/acetone, mp 246.00 °C: $(C_{18}H_{14}O_2)\cdot(C_{12}H_{12}N_2O)$, $M = 462.53$, orthorhombic, $a = 5.4581(2)$, $b = 7.9851(3)$, $c = 51.7327(16)$ Å, $V = 2254.69(14)$ Å^3, $T = 120(2)$ K, space group *Pbcn*, $Z' = 0.5$, $\mu(\text{Mo-K}\alpha) = 0.088$ mm^{-1}, size $0.20 \times 0.18 \times 0.08$ mm^3. 15411 total reflections of which 2201 were independent, 1638 observed $[I > 2\sigma(I)]$. Refinement against *F*2 with 211 parameters, $R1\ [I > 2\sigma(I)] = 0.0511$.

CCDC 238933–238935. See http://www.rsc.org/suppdata/cc/b4/b407510b/ for crystallographic data in .cif or other electronic format.

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