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REGULAR PAPER

Theoretical prediction of crystal structures of rubrene

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We theoretically predict crystal structures and molecular arrangements for rubrene molecule using CONFLEX program and compare them with the experimental ones. The most, second-most, and fourth-most stable predicted crystal structures show good agreement with the triclinic, orthorhombic, and monoclinic polymorphs of rubrene, respectively. The change in molecular conformation is also predicted between crystalline and gas phases: the tetracene backbone takes flat conformation in crystalline phase as in the observed structure. Meanwhile, it is twisted in gas phase. The theoretical prediction method used in this work provides the successful results on the determination of the three kinds of crystal structures and molecular arrangements for rubrene molecule. © 2014 The Japan Society of Applied Physics

1. Introduction

Organic semiconductors have a great potential for applications in the electronic devices such as field-effect transistors (FETs),[1,2] photovoltatic devices,[3] and light emitting diodes.[4] Advantages in organic devises, compared with inorganic ones, are flexibility, low-weight, easy and low-cost production, and so on. To realize high performance organic devices, the control and determination of molecular arrangements are quite important since the molecular arrangements affect physical and chemical properties such as charge carrier mobility.[5] Single crystals have often been used in organic FETs.[2] In non-crystalline states, it is considered that the molecular arrangements are correlated to their crystal structures.[6,7]

It is still a challenging subject to predict crystal structures theoretically from a given structural formula of a molecule.[8] Further a development of the prediction method is highly demanding in various areas. The establishment of the methodology will make possible to deduce the molecular arrangements and provide a useful theoretical tool for designing and synthesizing new semiconducting molecules for organic devices. Quite recently, one of the authors, Obata and his co-worker have developed a new theoretical prediction method of crystal structures for organic molecules which also allows change in molecular conformation.[9] This method was implemented in CONFLEX program.[10]

In the present work, we theoretically predict crystal structures and molecular arrangements of rubrene molecule (Fig. 1) by applying the newly developed prediction method. Rubrene has been extensively investigated as a typical organic FET material[2,11–17] and it shows the highest mobility of 40 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ among the organic semiconductors.[14] From the viewpoint of crystallography, this molecule has three polymorphs, that is, triclinic, monoclinic, and orthorhombic ones.[18,19] Therefore, the rubrene is suitable for examining the effectiveness of the theoretical prediction method for crystal structures. To our best knowledge, there is no previous work to apply the prediction of crystal structure to rubrene and related materials. We will show that the most, second-most, and fourth-most stable predicted crystal structures are in good agreement with the three experimental polymorphs, respectively.

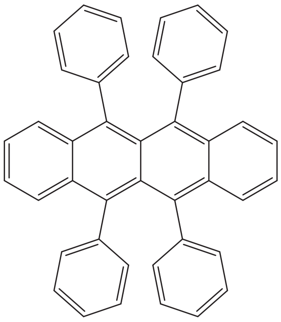

Fig. 1. Structural formula of rubrene.

2. Method

In crystallography, an asymmetric unit is defined as the smallest part of crystal structure from which, by applying symmetrical operations, the whole crystal space is covered. The replicas of the asymmetric unit generated by crystallographic symmetries are called as symmetry-related units in this paper. We performed the crystal structure predictions using CONFLEX program.[9,10] In the program, the crystal energy E_{crystal} is estimated by a molecular force field and expressed as

$$E_{\mathrm{crystal}} = E_{\mathrm{intra}} + \sum_{i}^{N}\sum_{S}^{M}\sum_{J}^{N} E_{\mathrm{inter}}(i;S,J). \qquad (1)$$

Here, E_{intra} is the sum of the intramolecular interaction energies in the molecule in a asymmetric unit and $E_{\mathrm{inter}}(i;S,J)$ is the interatomic interaction energy between atom i in the asymmetric unit and atom J in a symmetry-related unit S. N is the number of atoms in the asymmetry unit. M is the total number of symmetry-related units that we take into account: More explicitly speaking, the molecule in the S is included in the calculation when the closest interatomic distance between the molecules in the asymmetric unit and S is less than or equal to a cut-off radius R_{crystal}. In this work, R_{crystal} was set to 20 Å. Halgren's molecular mechanics Merck Molecular Force Filed 94 (MMFF94)[20] is employed as the molecular force field.

The prediction was performed along the following three steps: (i) generation of trial crystal structures, (ii) optimization of each trial, and (iii) comparison of the crystal energy

Table I. Crystal energies, structural parameters, and RMSD_{15} for the predicted and experimental crystal structures.

Polymorph	Rank[a)]	$\Delta E_{\mathrm{crystal}}$[b)] (kcal·mol^{-1})	Lattice parameters a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	RMSD_{15}[c)]
Tricli. ($P\bar{1}$)									
Predict.	1	0.00	7.326	8.769	12.298	94.80	106.50	95.05	0.343
Expt.[d)]			7.020(1)	8.543(1)	11.948(2)	93.04(3)	105.58(3)	96.28(3)	
Orth. ($Cmca$)									
Predict.	2	0.04	26.818	7.469	14.964	90.00	90.00	90.00	0.369
Expt.[e)]			26.828(4)	7.181(1)	14.306(2)	90.00	90.00	90.00	
Mono. ($P2_1/c$)									
Predict.	4	2.06	9.032	10.310	16.418	90.00	92.26	90.00	0.391
Expt.[d)]			8.740(1)	10.125(2)	15.635(3)	90.00	90.98(3)	90.00	
Mono. ($C2/c$)									
Predict.	3	0.62	7.362	27.497	14.852	90.00	94.40	90.00	

a) The rank n indicates the most n-th stable structure. b) The energies were represented as the difference from the energy value of predicted structure with the first rank. c) Root mean squared deviation of the carbon atomic positions, see text for details. d) Ref. 19. e) Ref. 18.

among the optimized structures. Before constructing trial crystal structures, an isolated molecule of rubrene was optimized in gas phase. This optimized molecular structure was rotated around the x-, y-, and z-axes. The trial crystal structures were generated by means of the oriented molecule as the asymmetric unit under a specified space group. The various rotation of the molecule produces a number of trials. We assumed three space group symmetries of Cc, $P2_1$, and $P1$. In this work, we generated total 5952 trials. Then, each trial crystal structure was subjected to the crystal-structure optimization. We optimized all the degree of freedom under the specified space group, that is, molecular arrangements between molecules, intramolecular structure as well as the unit cell dimensions. Note that the optimization of intramolecular structure allows a molecular deformation from the optimized structure in gas phase due to intermolecular interaction in a crystal state. We obtained 542 optimized structures since some of the trial structures resulted in the same optimized structures. Finally, the optimized structures were compared with respect to the crystal energies given in Eq. (1). The structures with low energies were selected as predicted crystal structures. The space groups and lattice parameters of the predicted crystal structures were redetermined using PLATON program.[21)]

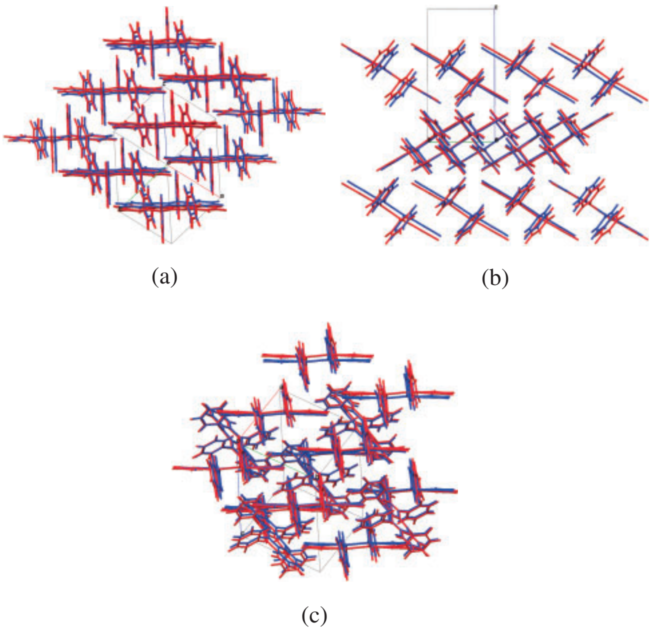

Fig. 2. (Color) Superposition of the predicted (red) and experimental[18,19)] (blue) crystal structures of rubrene. (a) Tricilinic, (b) orthorhombic, and (c) monoclinic polymorphs. The predicted structures have the lowest (a), second-lowest (b), and fourth-lowest (c) crystal energies, respectively.

3. Results and discussion

In Fig. 2, we show three predicted crystal structures with the lowest, second-lowest, and fourth-lowest crystal energies (shown in red). They belong to the triclinic (a), orthorhombic (b), and monoclinic (c) systems, respectively. In this figure, we superpose them with structures determined experimentally (shown in blue). We can see good agreement between the predicted and experimental structures in the three polymorphs.

Table I summarizes the crystal energies and the structural parameters for the predicted structures with the lowest four crystal energies. In this table, we also include available experimental data. The rank n in the table indicates the most n-th stable structure. RMSD_{15} is the root mean squared deviation of the carbon atomic positions for 15 molecules between the predicted and experimental crystal structures and was calculated using the Materials Module of Mercury.[22)] The lattice parameters in the predicted structures well reproduce the observed values. In addition, the values of RMSD_{15} are less than 0.4 Å for the three structures. These findings indicate that this theoretical prediction method provides the successful results on the determination of three kinds of crystal structures and molecular arrangements for rubrene molecule. The most deviation in the predicted cell parameters from the experimental values is 0.783 Å (5.0%) in length (c in the monoclinic polymorph) and 1.76° (1.9%) in angle (α in the triclinic polymorph).

Next, we examine the effects of packing forces on the molecular conformation in the crystalline phase. For this

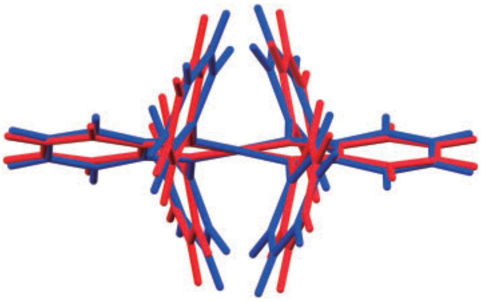

Fig. 3. (Color) Superposition of the molecular conformations of rubrene molecule in gas phase calculated by the MMFF94 (red) and DFT (blue).

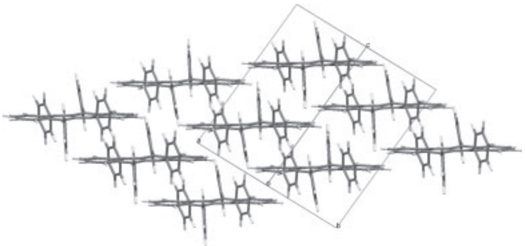

Fig. 4. Predicted crystal structure of rubrene with the third-lowest crystal energy.

purpose, we compare the molecular conformations of rubrene in gas phase and in crystal. The conformation in gas phase was determined by the MMFF94 force field as well as by a DFT calculation at the B3LYP/6-31G* level using Gaussian 09 package.[23] Figure 3 shows superposition of the molecular conformations calculated by the two methods. The root mean square deviation is 0.258 Å in the positions of the carbon atoms between these structures. As shown in Fig. 3, the tetracene backbone of rubrene takes twisted conformation in gas phase. On the other hand, our calculation predicts fairly flat conformation in crystalline phase as in the experimental structures (Fig. 2). This significant conformational change is induced by intermolecular interaction forces in the crystalline environment and is considered to contribute to stabilizing the crystal structure. In order to reliably predict the crystal structure of a flexible molecule like rubrene, it is essential to optimize molecular conformation in crystal state as implemented in CONFLEX program. From a more general point of view, we pointed out other two factors required for successful prediction: (i) the systematic generation of initial trials over possible molecular arrangements and (ii) the use of adequate molecular force field. The former is another characteristic feature in CONFLEX program.

Finally, we comment on the predicted structure with the third-lowest crystal energy. This structure is shown in Fig. 4 and its crystal energy and lattice parameters are listed in Table I. The polymorph corresponding to this structure has not been reported yet. The molecular arrangements in the polymorph is similar to that in the triclinic one [Figs. 2(a) and 4], and the difference of crystal energy between these structures is 0.62 kcal/mol. The low crystal energy may imply that the new polymorph exists, although we need further theoretical consideration on this structure.

4. Conclusion

We theoretically predicted crystal structures and molecular arrangements for rubrene molecule and compare them with the experimental ones. The most, second-most, and fourth-most stable predicted crystal structures show good agreement with the three experimental polymorphs, respectively. We also predicted the conformation change between crystalline and gas phases. The theoretical prediction method used in this work provides the successful results on the determination of the three kinds of crystal structures and molecular arrangements for rubrene molecule.

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