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Paraquat Substituent Effect on Complexation with a Dibenzo-24-crown-8-Based Cryptand

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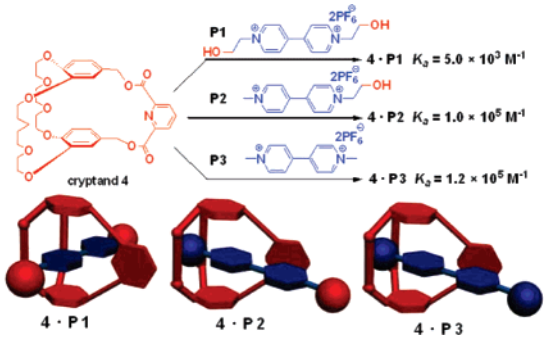

Dibenzo-24-crown-8-based cryptand **4** forms 1:1 inclusion complexes with three paraquat derivatives, **P1**, **P2**, and **P3**, as demonstrated by proton NMR spectroscopy and X-ray analysis. However, it was found that methyl-substituted paraquat derivatives, **P2** and **P3**, can bind cryptand **4** more strongly than non-methyl-substituted paraquat derivative **P1**. The association constants (K_a) were determined in acetone by using a UV−vis titration method to be 5.0×10^3 M^{-1} for **4·P1**, 1.0×10^5 M^{-1} for **4·P2**, and 1.2×10^5 M^{-1} for **4·P3**, respectively. In the solid state, **4·P2** and **4·P3** have similar T-type inclusion complexation conformations, which are very different from the pseudorotaxane-type complexation conformation of **4·P1**. Theoretical calculations were done to explain these experimental results.

In supramolecular chemistry, the control of the direction of incorporation of a guest into a host (or threading of a host onto a guest) and the relative positional changes that take place within the complexes is very important for the construction of molecular machines and preparation of information storage materials.[1] Fujita et al. observed that the guest rotation can be significantly restricted by the distortion of a cyclodextrin cavity.[1a] Schalley et al. found that small structural changes such as the simple exchange of a CH group by an isoelectronic N atom can cause unexpectedly large effects on the deslipping reaction of rotaxanes.[1d] Harada et al. revealed that the direction of threading cyclodextrins onto alkyl pyridinium derivatives can be kinetically controlled.[1j]

Paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) have been widely used as both hosts and guests in supramolecular chemistry.[2] The pursuit of high binding ability with paraquat derivatives and the facile synthesis of the precursors have led us to synthesize dibenzo-24-crown-8-based cryptands. Previously, we found that *cis*- and *trans*-dibenzo-24-crown-8-based cryptands form pseudorotaxane-type inclusion complexes with a bis(*β*-hydroxyethyl)-substituted paraquat salt **P1**.[3]

Here we report complexation studies between a *cis*-dibenzo-24-crown-8-based cryptand (**4**) and two methyl-substituted paraquat derivatives (**P2** and **P3**) and the comparison of these two complexes with the complex of cryptand **4** with **P1**. We found that methyl substitution can affect not only host−guest binding strength but also how the guest is incorporated into the host−guest inclusion complex in the solid state.

The *cis*-dibenzo-24-crown-8-based cryptand **4**[3] and paraquat derivatives **P1**,[4] **P2**,[5] and **P3**[6] with different *N*-substitutents were

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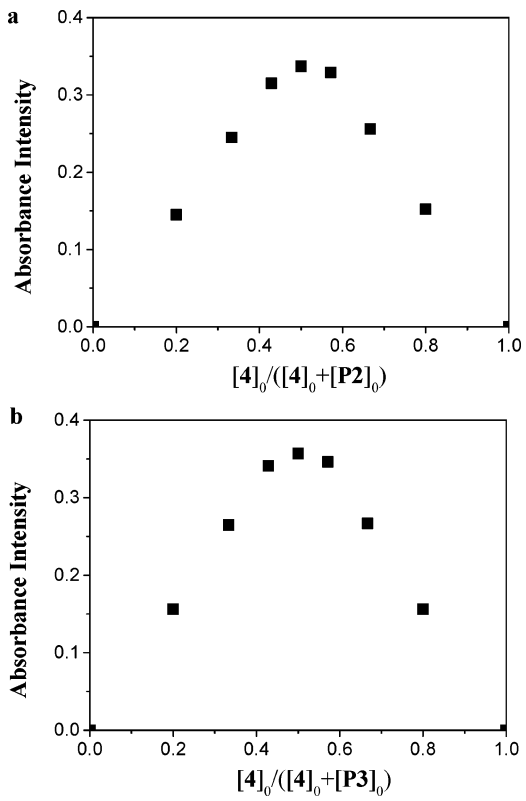
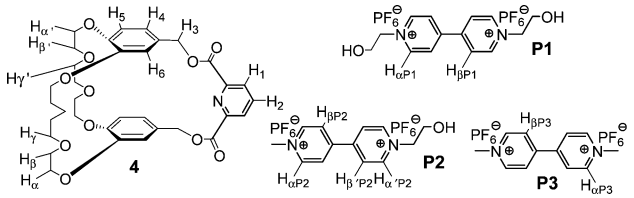


FIGURE 1. Job plots showing the 1:1 stoichiometries of the complexes between **4** and **P2** (a) and **4** and **P3** (b) in acetone by plotting the absorbance difference at $\lambda = 403$ nm (the host−guest charge-transfer band) against the mole fraction of **4**. $[\mathbf{4}]_0$, $[\mathbf{P2}]_0$, and $[\mathbf{P3}]_0$ are initial concentrations of **4**, **P2**, and **P3**. $[\mathbf{4}]_0 + [\mathbf{P2}]_0 = [\mathbf{4}]_0 + [\mathbf{P3}]_0 = 1.00$ mM.

synthesized by literature procedures. Then the complexation between crytand **4** and each of the three guests was studied. When equimolar (1.00 mM) acetone solutions of cryptand **4** and each of paraquat derivative salts **P1**, **P2**, and **P3** were made, a yellow color appeared due to charge transfer between electron-rich aromatic rings of the cryptand host and electron-poor pyridinium rings of the guest. And it was visually observed that the yellow color of the solution containing **P1** and cryptand **4** was not so deep as that of the other two solutions. This difference in the yellow color intensity gave us direct evidence that cryptand **4** binds **P1** not so strongly as it binds **P2** or **P3**.



Job plots[7] based on UV−vis spectroscopy absorbance data of the charge-transfer band ($\lambda = 403$ nm) demonstrated that the complexes of cryptand **4** with **P2** and **P3** were of 1:1 stoichiometry in solution (Figure 1). As reported previously,[3] the complex of cryptand **4** with **P1** also has a 1:1 stoichiometry in solution. The association constants were determined by probing the charge-transfer band of the complexes by UV−vis

(7) Job, P. *Ann. Chim.* **1928**, *9*, 113−203.

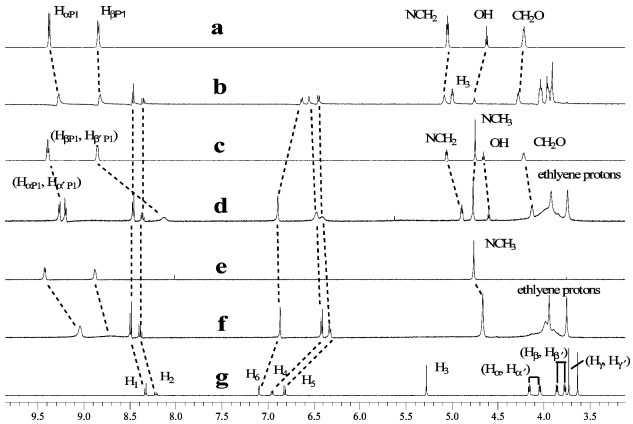


FIGURE 2. Partial proton NMR spectra (500 MHz, acetone-d_6, 22 °C) of **P1** (a), 2.00 mM cryptand **4** and **P1** (b), **P2** (c), 2.00 mM cryptand **4** and **P2** (d), **P3** (e), 2.00 mM cryptand **4** and **P3** (f), and cryptand **4** (g).

spectroscopy and employing a titration method. Progressive addition of an acetone solution with high guest salt (**P1**, **P2**, or **P3**) concentration and low host (**4**) concentration to an acetone solution with the same concentration of host **4** results in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data at $\lambda = 403$ nm with a nonlinear curve-fitting program afforded the corresponding association constants: 1.2 (±0.4) × 10^5 M^{-1} for **4·P3**, 1.0 (±0.3) × 10^5 M^{-1} for **4·P2**, and 5.0 (±0.2) × 10^3 M^{-1} for **4·P1**.[8,9] The large difference in association constants between complexes **4·P2** and **4·P3** and complex **4·P1** indicates that the methyl substitution has an important influence on the binding strength between *cis*-dibenzo-24-crown-8-based cryptand **4** and paraquat derivatives. This led us to further explore how the methyl substitution affects the host–guest complexation in solution by proton NMR spectroscopy, the host–guest organization in the solid state by single-crystal X-ray analysis, and why it has these effects by molecular modeling.

To investigate the complexation between cryptand **4** and the three paraquat derivatives, proton NMR spectra of equimolar (2.00 mM) deuterated acetone solutions of cryptand **4** with each of the three guests were examined. By comparison, it was found the spectra of solutions of **4** with **P2** and **P3** were different from that of the solution of **4** with **P1** (Figure 2). The peaks of some of the ethyleneoxy protons of cryptand **4** became broad after the complexation with methyl-substituted paraquat derivatives **P2** or **P3** (Figure 2, spectra d, f, and g), while clearly three peaks were observed for ethyleneoxy protons of cryptand **4** after complexation with **P1** (Figure 2, spectra b and g). Also β-pyridinium protons of **P2** and **P3** gave broad signals after complexation (Figure 2, spectra c, d, e, and f), while a relatively sharp peak was observed for β-pyridinium protons of **P1** after complexation (Figure 2, spectra a and b). On the basis of an

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(9) The association constant for **4·P1** obtained here is lower than the reported value,[3] 1.0 (±0.1) × 10^4 M^{-1}, which was determined based on ^{1}H NMR using the "Weber rule": Weber, G. *Molecular Biophysics*; Pullman, B., Weissbluth, M., Eds.; Academic Press: New York, 1965; pp 369−397.

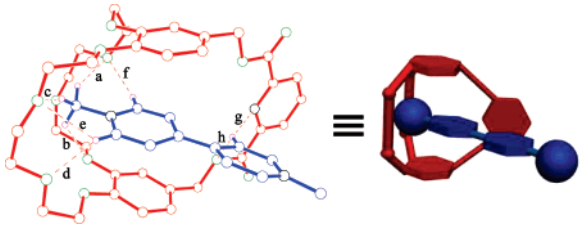

FIGURE 3. A ball-stick view of the X-ray structure of **4·P3**. **4** is red, **P3** is blue, hydrogens are magenta, oxygens are green, and nitrogens are black. PF_6 counterions, solvent molecules, and hydrogens except the ones involved in hydrogen bonding between **4** and **P3** were omitted for clarity. Hydrogen bond[12] parameters: H···O (N) distance (Å), C−H···O (N) angle (deg), C···O (N) distance (Å)—**a**, 2.623, 149.6, 3.503; **b**, 2.507, 129.2, 3.217; **c**, 2.431, 157.1, 3.356; **d**, 2.262, 147.4, 3.105; **e**, 2.669, 135.1, 3.408; **f**, 2.388, 153.3, 3.266; **g**, 2.461, 141.5, 3.259; **h**, 2.652, 135.7, 3.397. The centroid−centroid distance (Å) and dihedral angle (deg) between the two catechol rings of cryptand **4**: 6.741, 16.64.

HMQC spectrum of a solution of **4** and **P2** (see the Supporting Information) and integration, the singlet at δ 4.76 ppm in Figure 2d can be assigned to the *N*-methyl protons of **P2**. Similarly the singlet at δ 4.66 ppm in Figure 2f can be assigned to the *N*-methyl protons of **P3**. The singlet for the benzylic protons H_3 of cryptand **4** disappeared after complexation with **P2** and **P3** (Figure 2, spectra d, f, and g).[10] However, the singlet for the benzylic protons H_3 of cryptand **4** was observed at δ 4.99 ppm after complexation between **4** and **P1** (Figure 2, spectra b and g).[11]

X-ray analyses were done on single crystals of complexes obtained by vapor diffusion of pentane into acetone solutions of cryptand **4** and each of the three paraquat derivative guests. In the solid state, **4·P2** and **4·P3** have similar T-type conformations, which are very different from the pseudorotaxane-type conformation of **4·P1**.[3]

In the crystal structure of 1:1 complex **4·P3** (Figure 3), the *N*-methyl group of paraquat guest **P3** is oriented into the dibenzo-24-crown-8 cavity and the complex has a T-type conformation. Complex **4·P3** is stabilized by eight hydrogen bonds. All three *N*-methyl hydrogen atoms of paraquat **P3** form effective hydrogen bonds with the ethyleneoxy oxygen atoms (**a**, **b**, and **c** in Figure 3) of cryptand **4**. Also two α-pyridinium hydrogen atoms form three hydrogen bonds with the ethyleneoxy oxygen atoms of the host (**d**, **e**, and **f** in Figure 3). One β-pyridinium hydrogen atom forms two hydrogen bonds with the pyridine nitrogen atom (**g** in Figure 3) and an ester oxygen atom on the host (**h** in Figure 3), respectively. Complex **4·P3** is stabilized also by face-to-face π-stacking and charge transfer interactions between the two electron-rich aromatic rings of the host and one of the two electron-poor pyridinium rings of the guest. The two catechol rings of host **4** are not parallel but rather have a dihedral angle of 16.64° and a centroid−centroid distance of 6.741 Å (Figure 3).

(10) It has been known for some time that some complexes of lariat ethers (Durst, H. D.; Echegoyen, L.; Gokel, G. W.; Kaifer, A. *Tetrahedron Lett.* **1982**, *23*, 4449−4452. Echegoyen, L.; Parra, D.; Bartlotti, L. J.; Hanlon, C.; Gokel, G. W. *J. Coord. Chem.* **1988**, *18*, 85−91) and cryptands (Schmidt, E.; Popov, A. I.; Kintzinger, J. P.; Tremillon, J.-M. *J. Am. Chem. Soc.* **1983**, *105*, 7563−7566) display increased relaxation times, due to both "compression" and desolvation and the relaxation process being dominated by reorientational motion of the total complex. We hypothesize that this is the basis of the disappearance of the signal for the benzylic protons **4·P2** and **4·P3**.

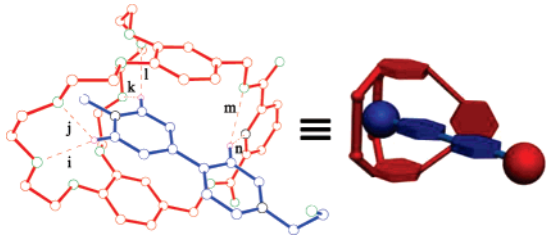

FIGURE 4. A ball-stick view of X-ray structure of **4·P2**. **4** is red, **P2** is blue, hydrogens are magenta, oxygens are green, and nitrogens are black. PF_6 counterions, solvent molecules, and hydrogens except the ones involved in hydrogen bonding between **4** and **P2** were omitted for clarity. Hydrogen bond[12] parameters: H···O (N) distance (Å), C−H···O (N) angle (deg), C···O (N) distance (Å)—**i**, 2.350, 3.221, 152.0, **j**, 2.424, 133.6, 3.155, **k**, 2.557, 140.3, 3.344, **l**, 2.580, 149.7, 3.434, **m**, 2.556, 141.9, 3.354, **n**, 2.457, 142.2, 3.259. The centroid−centroid distance (Å) and dihedral angle (deg) between the two catechol rings of cryptand **4**: 6.740, 14.20.

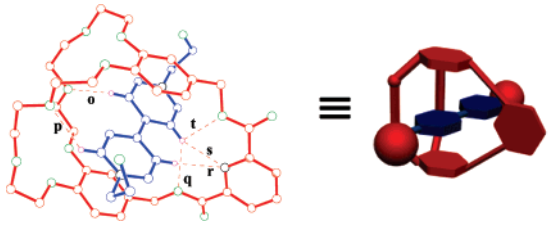

FIGURE 5. A ball-stick view of X-ray structure of **4·P1**.[3] **4** is red, **P1** is blue, hydrogens are magenta, oxygens are green, and nitrogens are black. PF_6 counterions, solvent molecules, and hydrogens except the ones involved in hydrogen bonding between **4** and **P1** were omitted for clarity. Hydrogen bond[12] parameters: H···O (N) distance (Å), C−H···O (N) angle (deg), C···O (N) distance (Å)—**o**, 2.317, 130.6, 3.023; **p**, 2.347, 133.9, 3.082; **q**, 2.535, 131.1, 3.239; **r**, 2.703, 175.9, 3.651; **s**, 2.402, 159.2, 3.307; **t**, 2.653, 101.1, 2.986. The centroid−centroid distance (Å) and dihedral angle (deg) between the two catechol rings of cryptand **4**: 6.890, 9.89.

The *N*-methyl group of paraquat guest **P2** is also oriented into the dibenzo-24-crown-8 cavity in the crystal structure (Figure 4) of the 1:1 complex **4·P2** in a T-type conformation similar to **4·P3** in the solid state. Complex **4·P2** is also stabilized by hydrogen bonding and face-to-face π-stacking and charge transfer interactions between the two electron-rich aromatic rings of host and one of the two electron-poor pyridinium rings of the guest. Also two α-pyridinium hydrogens are hydrogen bonded to ethyleneoxy oxygen atoms (**i**, **j**, **k**, and **l** in Figure 4) and one β-pyridinium hydrogen atom forms two hydrogen bonds with the pyridine nitrogen atom (**n** in Figure 4) and an ester oxygen atom on the host (**m** in Figure 4). However, none of the three methyl hydrogen atoms of **P3** are involved in hydrogen bonding between the host and guest (Figure 4). The two catechol rings are not parallel but rather have a dihedral angle of 14.20° and a centroid−centroid distance of 6.740 Å, which are very close to the above-mentioned corresponding values, 16.64° and 6.741 Å, for **4·P3**.

As reported previously, in the solid state, the 1:1 complex **4·P1** (Figure 5)[3] has a pseudorotaxane-type conformation, which is significantly different from the above-mentioned T-type conformations of **4·P3** and **4·P2** in the solid state (Figures 3 and 4). Here non-methyl-substituted paraquat derivative guest

(11) The different behavior must be a consequence of the differing structures of the complexes; see the discussion of Figures 3−5.

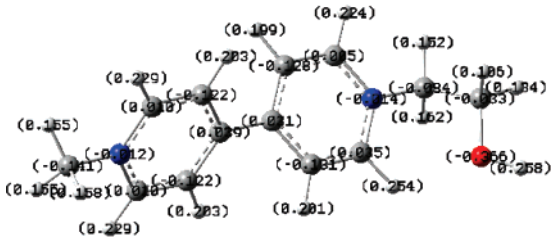

FIGURE 6. Distribution map of the Mulliken charges of **P2** at the AM1 level as determined with the Gaussian program. Carbons are gray, nitrogens are blue, hydrogens are white, and oxygen is red.

P1 is symmetrically threaded into the cavity of cryptand host **4** (Figure 5). None of the hydrogen atoms on the two hydroxyethyl groups of guest **P1** are involved in hydrogen bonding between the host and guest. Both of the electron-poor pyridinium rings of the guest are involved in face-to-face π-stacking and charge transfer interactions with the two catechol rings of cryptand host **4** (Figure 5), but only one of the two electron-poor pyridinium rings of the guest is involved in these kinds of interactions with the two catechol rings of cryptand host **4** for **4·P3** and **4·P2** (Figures 3 and 4). The dihedral angle and centroid−centroid distance of the two catechol rings of cryptand host **4** are 9.89° and 6.890 Å, which are very different from the above-mentioned corresponding values, 16.64° and 6.741 Å for **4·P3** and 14.20° and 6.740 Å for **4·P2**.

Therefore, it was discovered that *N*-methyl substitution can affect not only host−guest binding strength, but also the geometry of guest inclusion in the complex in the solid state. To explain these experimental results, theoretical calculations were done. Distribution maps (the one for **P2** is shown in Figure 6) of the Mulliken charges of **P1**, **P2**, and **P3** were calculated at the AM1 level with the Gaussian program. It is obvious that both pyridinium rings of these paraquat derivatives are very electron-poor (Figure 6), so they can have face-to-face π-stacking and charge transfer interactions with the two catechol rings of cryptand host **4**. All of their pyridinium, *N*-methyl, and *N*-methylene hydrogens have some kind of positive charge (Figure 6). Therefore, these hydrogens are capable of forming hydrogen bonds with electron-rich atoms, such as the ethyleneoxy oxygen and pyridine nitrogen atoms of host **4**. When the paraquat derivative guest has an *N*-methyl group, this methyl group prefers to stay in the cavity of the dibenzo-24-crown-8 ring because in this way seven (three *N*-methyl, two α-pyridinium, and two β-pyridinium hydrogens) of these hydrogens can form hydrogen bonds with electron-rich atoms of cryptand **4**. In contrast only six of these hydrogens (two α-pyridinium and four β-pyridinium hydrogens) can form hydrogen bonds in the pseudorotaxane-type complex conformation. Here the size of the dibenzo-24-crown-8 ring is appropriate so that all three *N*-methyl hydrogens can be involved in hydrogen bonding between the host and guest and $N^+\cdots O$ interactions can form.[13] When the paraquat derivative guest does not have an *N*-methyl group, only six of these hydrogens (two *N*-methylene, two α-pyridinium, and two β-pyridinium hydrogens) can form hydrogen bonds with electron-rich atoms no matter whether the complex has a T-type conformation or a pseudorotaxane-type conformation. However, the electron-rich catechol rings can have face-to-face π-stacking and charge transfer interactions with both electron-poor pyridinium rings when the complex has a pseudorotaxane-type conformation, while they can do this with only one electron-poor pyridinium ring when the complex has a T-type conformation. Therefore, methyl-substituted paraquat derivatives **P2** and **P3** form T-type inclusion complexes with cryptand host **4**, but non-methyl-substituted paraquat derivative **P1** forms a pseudorotaxane-type inclusion complex with cryptand host **4**. More acidic hydrogens can form hydrogen bonds with the electron-rich atoms of cryptand host **4** when the paraquat derivative guest is methyl-substituted. Therefore, $K_{a,4\cdot P3}$ and $K_{a,4\cdot P2}$ are more than 19 times $K_{a,4\cdot P1}$.

In summary, we studied the complexation of the dibenzo-24-crown-8-based cryptand **4** with three paraquat derivatives **P1**, **P2**, and **P3** with different *N*-substituents. Proton NMR spectroscopy, UV−vis spectroscopy, X-ray analysis and molecular modeling were used to study the substituent influence on their complexation. It was found that methyl-substitution can affect not only binding strength but also how the guest is incorporated into the complex. Theoretical calculations are consistent with these experimental results. The studies presented here provided useful information for improving host−guest binding strength and controlling the host−guest complex conformation by simple substitution.

Experimental Section

The *cis*-dibenzo-24-crown-8-based cryptand **4**[3] and paraquat derivatives, **P1**,[4] **P2**,[5] and **P3**,[6] were all synthesized by literature procedures. All solutions for proton NMR study of complexations were prepared as follows. Precisely weighed amounts of dried compounds were added into screw cap vials. Acetone-d_6 was added with to-deliver volumetric pipets. Then specific volumes of each fresh solution were mixed to yield the desired concentrations. For example, to prepare a solution of 2.00/2.00 mM **4**/**P1**, 0.500 mL of 4.00 mM **4** and 0.500 mL of 4.00 mM **P1** were added into a screw cap vial with 0.500 mL to-deliver pipets. ^{1}H NMR data were collected on a temperature-controlled 500 MHz spectrometer. The general procedure for the determination of the association constants for all complexes is described in the Supporting Information.

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Supporting Information Available: Determination of association constants of **4·P1**, **4·P2**, and **4·P3**, HMQC spectrum of a solution of **4** and **P2**, X-ray analysis data of **4·P2**, X-ray analysis data of **4·P3**, thermal ellipsoid plots of the X-ray crystal structures of **4·P1**, **4·P2**, and **4·P3**, and calculations of distribution maps of the Mulliken charges of **P1** and **P3** at the AM1 level. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Here a hydrogen bond is thought to exist when H···O (N) distance is less than the sum, 2.72 (2.75) Å, of van der Waals radii (Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451) of the hydrogen atom and the acceptor O (N) atom, and the C−H···O (N) angle is greater than 90°. This method of determination of the existence of hydrogen bonds is traditionally accepted though it was challenged by some people (Aakeröy, C. B.; Evans, T. A.; Seddon, K. R.; Pálinkó, I. *New J. Chem.* **1999**, *23*, 145−152. van den Berg, J.-A.; Seddon, K. R. *Cryst. Growth Des.* **2003**, *3*, 643−661). However, this method is simple and efficient. To the best of our knowledge, there is not a method better than this one. A wealth of structural and spectroscopic data revealed that C−H···O hydrogen bonds have H···O distances from 2.0 to 3.0 Å, C···O distances from 3.0 to 4.0 Å, and C−H···O angles from 90° to 180° (Raymo, F. M.; Bartberger, M. D.; Houk, K. N.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 9264−9267).

(13) Loeb, S. J.; Wisner, J. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2838−2840.