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Modeling Molecule-in-a-Crystal: The Case of Push−Pull Quinonoids

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Structural modifications that molecules undergo when they assemble into the crystalline state are important indicators of the microenvironment in the molecular crystal. An accurate appraisal of the molecule-in-a-crystal can provide critical inputs for drawing correlations between molecular structure/properties and material attributes, an essential prerequisite for the design of novel molecular materials. A pertinent case would be the evaluation of local field factors for the computation of nonlinear optical (NLO) susceptibilities of crystals from molecular hyperpolarizabilities.[1] The starting point for the description of the molecule-in-a-crystal is the modeling of its structure, especially those features which dominate the molecular contribution to the material properties. Such computations are complicated by the coexistence of a variety of intermolecular interactions.[2] A popular approach is to use embedding models[3] wherein the effect of the lattice around a molecule is assessed using crystal structure information and computed interaction energies. The modifications of molecular structure by the crystal forces are often subtle, rendering the computational description difficult. Therefore, molecules which undergo large structural changes between the isolated state and the crystal environment are of special interest. Conformational changes of molecules in solutions and enzyme active sites are commonly modeled using implicit solvation models.[4] The medium effects on large geometry changes of donor−acceptor complexes[5] and the crystal structure geometry of a transition state analogue[6] have been replicated using computations including solvation effects. Unlike the embedding models, this approach does not require the crystal packing information. We have observed in a class of formally quinonoid push−pull molecules a prominent difference between their structure in the crystalline state and the computed geometry describing the isolated molecule. In this Communication we demonstrate that the role of the crystal lattice in this structural modification can be mimicked using solvation modeling within semiempirical quantum chemical calculations. More significantly, the dielectric constant used in the solvation calculation is a convenient descriptor of the environment of the molecule. The approach is tested further using crystal structure and computational investigations of a new member of the family having a highly ionic and hydrated structure. The solvation modeling provides a unified description of the variety of intermolecular interactions manifested by this class of molecular crystals.

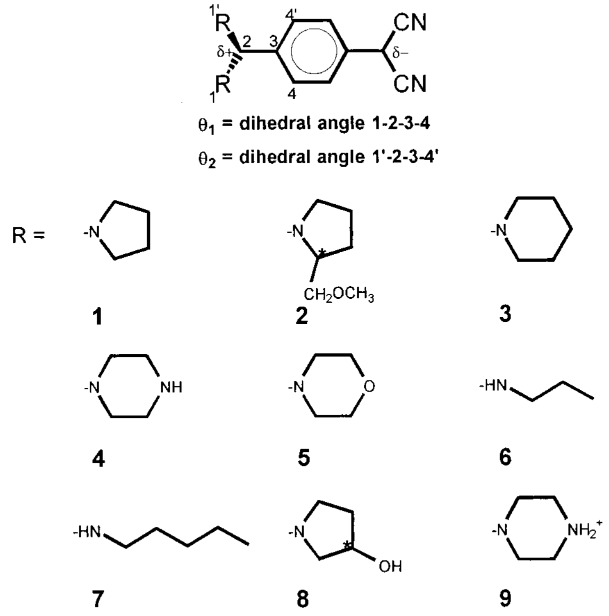

Figure 1. Molecules considered in the study; the angle θ in the text is the average of θ_1 and θ_2 shown.

Earlier studies in our laboratory have shown that diaminodicyanoquinodimethanes (Figure 1) possess strong second-order NLO properties.[7−11] Crystallographic studies of these molecules reveal a large dihedral twist, θ, between the diaminomethylene unit and the aromatic ring plane, a consequence of the steric interaction between the amino group substituents and the ortho H atoms of the ring. This twist leads to zwitterionic benzenoid character and a large dipole moment.[7,12] Computational studies[9,13] have shown that the excitation energy and hyperpolarizability of these

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(1) Zyss, J.; Chemla, D. S. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 1, p 23.

(2) (a) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82,* 1. (b) Desiraju, G. R. *Crystal Engineering, The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (c) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27,* 309. (d) Gavezzotti, A. *Crystallogr. Rev.* **1998**, *7,* 5.

(3) (a) Braga, D.; Grepioni, F. *Organometallics* **1991**, *10,* 1254. (b) Stockton, G. W.; Godfrey, R.; Hitchcock, P.; Mendelsohn, R.; Mowery, P. C.; Rajan, S.; Walker, A. F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2061. (c) Craw, J. S.; Greatbanks, S. P.; Hillier, I. H.; Harrison, M. J.; Burton, N. A. *J. Chem. Phys.* **1997**, *106,* 6612.

(4) Cremer, C. J.; Truhlar, D. J. *Chem. Rev.* **1999**, *99,* 2161.

(5) Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116,* 7429; see also refs 1−4 therein.

(6) Sherer, E. C.; Yang, G.; Turner, G. M.; Shields, G. C.; Landry, D. W. *J. Phys. Chem. A* **1997**, *101,* 8526.

(7) Ravi, M.; Radhakrishnan, T. P. *J. Phys. Chem.* **1995**, *99,* 17624.

(8) Ravi, M.; Rao, D. N.; Cohen, S.; Agranat, I.; Radhakrishnan, T. P. *J. Mater. Chem.* **1996**, *6,* 1853.

(9) Ravi, M.; Rao, D. N.; Cohen, S.; Agranat, I.; Radhakrishnan, T. P. *Chem. Mater.* **1997**, *9,* 830.

(10) (a) Gangopadhyay, P.; Sharma, S.; Rao, A. J.; Rao, D. N.; Cohen, S.; Agranat, I.; Radhakrishnan, T. P. *Chem. Mater.* **1999**, *11,* 466. (b) Sharma, S.; Radhakrishnan, T. P. *Mol. Cryst. Liq. Cryst.* **2000**, *338,* 257.

(11) Ravi, M.; Gangopadhyay, P.; Rao, D. N.; Cohen, S.; Agranat, I.; Radhakrishnan, T. P. *Chem. Mater.* **1998**, *10,* 2371.

(12) Kagawa, Y.; Szablewski, M.; Ravi, M.; Ann Lackman, N.; Cross, G. H.; Bloor, D.; Batsnor, A. S.; Howard, J. A. K. *Nonlinear Opt.* **1999**, *22,* 235.

(13) Gangopadhyay, P.; Ravi, M.; Radhakrishnan, T. P. *Ind. J. Chem.* **2000**, *39A,* 106.

10.1021/cm010071c CCC: $20.00

Table 1. Twist Angles of Molecules in Figure 1 from single crystal analysis, θ_{cryst}, the AM1 computed values, θ_0, and the AM1/COSMO computed values, θ_ϵ, which show the best agreement with θ_{cryst} and the corresponding ϵ[a]

molecule	θ_{cryst} (deg) [ref]	θ_0 (deg)	θ_ϵ (deg)	ϵ
1	55.2 [8]	58.2		
2	54.1 [9]	57.5		
3[b]	46.6 [14]	30.2	45.7	2
4[b]	42.9 [14]	28.3	44.8	2
5	48.3 [14]	24.5	48.8	3
6	47.0 [10]	28.0	45.7	3
7	47.1 [10]	29.3	47.1	3
8	73.8 [11]	58.7	73.9	8
9	52.4 [this work]	1.4	54.5	20

[a] The θ values shown are the average of the two dihedral angles (Figure 1) in these bis-substituted systems. [b] There are two molecules in the crystallographic asymmetric unit with very similar θ values; the average is provided.

molecules and hence their solid-state NLO properties are very sensitive to θ. The twist angles, θ_{cryst}, from single-crystal X-ray studies are collected in Table 1. The twist angle, θ_0, from geometry optimization using the AM1[15] semiempirical method shows good agreement with θ_{cryst} only in **1** and **2** (Table 1); in **3**−**8**, the θ_{cryst} values are considerably higher. The enhanced θ_{cryst} of **8** compared to **1** and **2** has been attributed to extensive intermolecular H-bonding.[11]

The discrepancy between the computed and experimental values of θ points to the role of the polar microenvironment in the crystal lattice (cf. ref 5) which stabilizes the zwitterionic form. Recently, we have modeled the solvent selection of polymorphs in a molecular crystal using AM1/COSMO calculations on supramolecular clusters.[16] We hypothesized that the crystalline environment can be mimicked using the dielectric continuum model used in the solvation calculation, COSMO.[17] Full geometry optimization of **1**−**8** starting with the AM1 geometries above and invoking different dielectric constants, ϵ, within the solvation model[18] showed that, even at low ϵ, θ_ϵ is higher than θ_0. Generally, θ_ϵ increases with ϵ and saturates at higher values (Figure 2). The θ_ϵ values which agree best with θ_{cryst} and the corresponding ϵ are collected in Table 1; the rest of the computed molecular geometry at this ϵ also agrees well with the experimental geometry. As noted earlier, **1** and **2** require no solvation modeling, implying that the dihedral twist is essentially a feature of the isolated molecule. The low values of ϵ required for **3**−**7** are suggestive of a weakly polarizable molecular environment arising from nominal intermolecular interactions. Intermolecular H-bonding has been observed in **6**[10a] and **7**,[10b] and $\epsilon = 4$ also reproduces the correct twist angle in these crystals. The higher value of ϵ required in the case of **8** appears to reflect the impact of the extensive H-bonding interactions.[11]

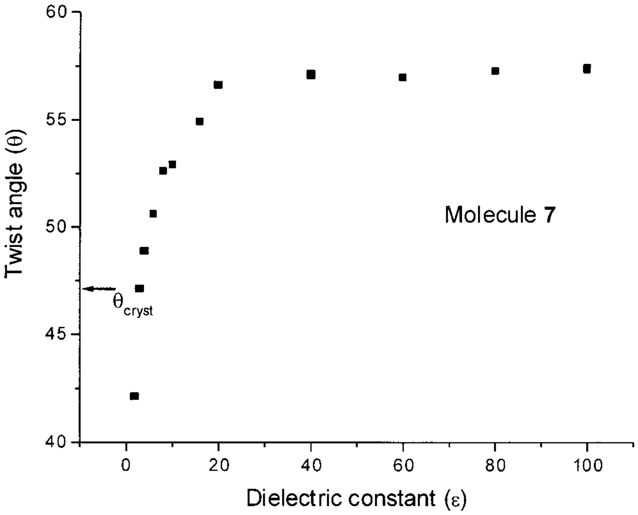

Figure 2. AM1/COSMO calculated twist angle as a function of the dielectric constant employed in the calculation for molecule **7** in Figure 1. The twist angle obtained from crystal structure analysis, θ_{cryst}, is indicated.

As a further test of this modeling we have examined the crystal structure of a new member of the family. The bis(*p*-toluenesulfonate) salt of 7,7-bis(piperazinium)-8,8-dicyanoquinodimethane (**9**) was prepared by the addition of *p*-toluenesulfonic acid to **4**. Crystals of **9**-(pTS)$_2$ grown from water belong to the *P*2/*c* space group with half the molecule and 2.5 water molecules in the asymmetric unit.[19] Extended H-bonding involving the piperazinium, cyano, and sulfonate groups and water molecules produces supramolecular squares and rectangles in this crystal. The view along the *b* axis (Figure 3) shows the molecular twist in **9**. It shows also the distribution of pTS$^-$ ions and water molecules around the push−pull quinonoid moiety that leads to a highly polar environment. Interestingly, AM1 calculations on **9** showed a negligible θ_0 of 1.4°. This planarization results from the destabilization of the positive charge at the diaminomethylene end of the zwitterionic form due to the protonation on the piperazine moieties. In the AM1/COSMO optimization, the θ remains 1.4° till $\epsilon = 15$ and suddenly increases thereafter. The experimental angle is recovered at $\epsilon = 20$ (Table 1). The large enhancement of θ and its modeling using a high ϵ reflect the strongly ionic microenvironment and the abundant H-bonded water molecules in **9**-(pTS)$_2$.

The present study demonstrates that the molecular structure modification occurring in a crystal environment can be conveniently modeled using solvation-included geometry optimization at the semiempirical level. Such an analysis also provides useful insight into the microscopic dielectric constant experienced by the molecule and should be of utility in evaluating accurately the molecular contribution to crystal properties. Assuming a typical refractive index of 1.5−2.0, the

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(14) Ravi, M.; Cohen, S.; Agranat, I.; Radhakrishnan, T. P. *Struct. Chem.* **1996**, *7*, 225.

(15) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. The MOPAC93 (Fujitsu Inc.) program was used; starting with the molecular structure from crystal structure analysis, geometries were fully optimized using the EF and PRECISE keywords; calculation of the full potential energy surface for $\theta = 0-90°$ gave minima identical to these optimized geometries. Test calculation at the ab initio B3LYP/6-31G* level on **6** gave $\theta = 29.0°$ in good agreement with the AM1 results.

(16) Sharma, S.; Radhakrishnan, T. P. *J. Phys. Chem. B* **2000**, *104*, 10191.

(17) Klamt, A.; Shüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799.

(18) Full geometry optimization invoking EF, PRECISE, NSPA=60, and the values of EPS mentioned in the text. Test calculations on **6** at the B3LYP/6-31G* level including solvation correction (CPCM) with ether ($\epsilon = 4.3$) gave $\theta = 35.4°$. $\theta_\epsilon > \theta_0$, as in the AM1 calculations; however, a higher ϵ appears to be necessary to reproduce θ_{cryst}.

(19) Crystal data for **9**-(pTS)$_2$: monoclinic, *P*2/*c*, *a* = 9.659 (3), *b* = 12.798 (4), *c* = 16.185 (2) Å, β = 104.054 (18)°, 298 K, Z = 2, R = 0.0496, GOF = 1.016.

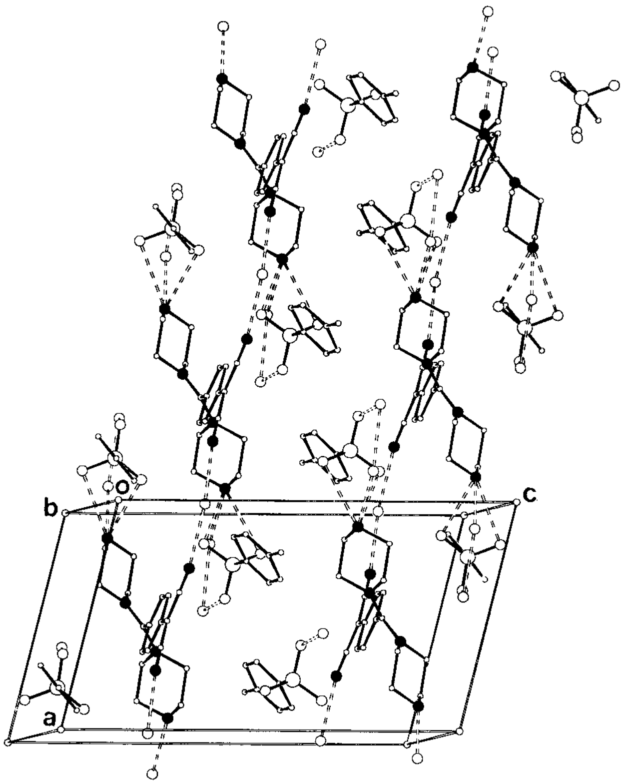

Figure 3. Crystal structure of **9**-$(pTS)_2$ from single-crystal X-ray analysis showing the molecular array parallel to the *ac* plane. H atoms are omitted for clarity; C (◦), N (●), O (o), and S (○) are indicated; H-bonds are shown as broken lines (= = =).

dielectric constant of organic crystals at optical frequencies will be of the order of 2−4. The ϵ values needed in the semiempirical solvation calculations are in this range for most of the systems. The larger ϵ required for **8** is compatible with the fact that the dielectric constants of compounds with extensive H-bonding are generally higher.[20] The still larger ϵ in the case of **9** reflects the highly polarizable molecular environment made up of several H-bonded water molecules. A basic question arises at this point: does the observed structure modification occur when the molecule is in a solvated state or when it associates with others initiating the crystal assembly, and which of these states is the solvation calculation really modeling? In the case of the push−pull quinonoid systems a tentative answer can be offered. Computational studies noted earlier[13] have shown that the excitation energy decreases monotonically with increasing θ. However, the electronic absorption data of **1**−**9** (Table 2) do not indicate any clear correlation between the absorption maxima in solutions and the θ_{cryst}. This suggests that the structural modification observed in the crystalline state is not initiated when the isolated molecule is in solution but occurs when the supramolecular assembly leading to the crystal is formed. It also indicates that the current solvation calculations actually model the crystalline environments. A logical extension of this study would be the modeling of electronic structure and properties of molecules in the crystal; preliminary explorations suggest that this is a promising approach. Solvation-included quantum chemical computations should prove to be a powerful and convenient tool to study different aspects of the molecule-in-a-crystal.

Table 2. Twist Angles, θ_{cryst}, of Molecules in Figure 1 and the Peak Position in the Absorption Spectra of Their Solutions in Methanol, Acetonitrile, and Tetrahydrofuran

		λ_{max} (nm)		
molecule	θ_{cryst} (deg)	methanol	acetonitrile	THF
4	42.9	414	415	461
3	46.6	405	414	460
6	47.0	362	380	414
7	47.1	363	378	414
5	48.3	423	420	462
9	52.4	422	450	459
2	54.1	398	406	449
1	55.2	366	375	431
8	73.8	372	388	434

[a] The entries are ordered according to increasing θ_{cryst}.

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Supporting Information Available: Crystal structure of **9**-$(pTS)_2$ and results of semiempirical and ab initio studies for **1**−**9** (24 pages) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Schweitzer, R. C.; Morris, J. B. *Anal. Chim. Acta* **1999**, *384*, 285.