Published in final edited form as:

J Phys Chem A. 2012 August 2; 116(30): 8100–8105. doi:10.1021/jp3050274.

A Reinvestigation of the Dimer of para-Benzoquinone with Pyrimidine with MP2, CCSD(T) and DFT using Functionals including those Designed to Describe Dispersion

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Abstract

We reevaluate the interaction of pyridine and p-benzoquinone using functionals designed to treat dispersion. We compare the relative energies of four different structures: stacked, T-shaped (identified for the first time) and two planar H-bonded geometries using these functionals (B97-D, ω B97x-D, M05, M05-2X, M06, M06L, M06-2X), other functionals (PBE1PBE, B3LYP, X3LYP), MP2 and CCSD(T) using basis sets as large as cc-pVTZ. The functionals designed to treat dispersion behave erratically as the predictions of the most stable structure vary considerably. MP2 predicts the experimentally observed structure (H-bonded) to be the least stable, while single point CCSD(T) at the MP2 optimized geometry correctly predicts the observed structure to be most stable. We have confirmed the assignment of the experimental structure using new calculations of the vibrational frequency shifts previously used to identify the structure. The MP2/cc-pVTZ vibrational calculations are in excellent agreement with the observations. All methods used to calculate the energies provide vibrational shifts that agree with the observed structure even though most do not predict this structure to be most stable. The implications for evaluating possible π -stacking in biologically important systems are discussed.

Keywords

Pi-Stacking; Hydrogen-Bonding; Dispersion-corrected Functionals

Interactions due to dispersion and/or induction may play important roles in the energetics of biological molecules, such as DNA and peptides. The stacking interactions of the DNA bases have received considerable attention.^{1,2,3} From studies of protein databases, π -stacking is thought to be common in proteins,⁴ and both tryptophane and phenylalanine have been reported to be important in short peptide sequences thought to be essential for amyloid formation. We shall report elsewhere that these two residues enhance the formation of parallel β -sheets even when present as single mutations in all alanine sheets, where π -stacking cannot occur.

The energetic contribution to π -stacking due to dispersion forces needs to be better understood. MP2 and/or CCSD(T) calculations are often used to calculate such interactions

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as Hartree-Fock and the more common functionals, such as B3LYP, are not capable of accounting for pure dispersion interactions. Several functionals have recently been developed with the specific purpose of properly accounting for dispersion.

The primary purpose of this paper is to compare some of these functionals with both experimental and higher level calculations. We have recently evaluated the behavior of several of these for purely dispersive, induction/dispersion⁵ and H-bonding interactions,⁶ and prediction of peptide structures.⁷ In this paper, we examine their behavior compared with MP2 and CCSD(T) calculations on the complex formed between pyrimidine and p-benzoquinone, for which detailed experimental evidence has been reported.⁸

Both dispersion and induction interactions depend upon the size of the basis sets used with MP2 or CCSD(T) calculations when nucleocentric atomic bases are used due to the fact that the individual functions are spherical harmonics which cannot be individually polarized. The polarization arrives via the overlap populations, which have greater flexibility as the basis set is increased. Accurate CCSD(T) and MP2 calculations rapidly become excessively expensive as the size of the system increases. Recently, several new functionals have been developed that attempt to properly deal with these interactions.

Basis set superposition error (BSSE) can easily be confused with dispersion or induction interactions. An experimental study of the hetero-dimer of pyrimidine and p-benzoquinone isolated in an Argon matrix concluded that the H-bonded structure (Planar B) predominated, while accompanying MP2/6-31++G** calculations showed that the preference for stacked vs Hbonded dimers is inverted when BSSE is considered. According to this report, the π -stacked dimer is incorrectly predicted to be more stable than the experimentally determined H-bonding dimer before (but not after) counterpoise (CP) correction.⁸ Sadlej has reinvestigated this result using MP2 and symmetry-adapted perturbation theory (SAPT) with the aug-cc-pVDZ basis set.⁹ Her report shows the results depend upon the method of calculation and whether (or not) the geometry optimization uses a CP-corrected surface.

If one attempts to calculate the interaction energy between two rare gas atoms via geometry optimization at the HF level with a moderate sized basis set, one finds a minimum on the potential energy surface despite the fact that HF calculations are incapable of describing the dispersion interaction. This minimum will disappear at the Hartree-Fock limit (complete basis set) or if the optimization be carried out on a surface that is corrected for BSSE using the (CP) correction^{10,11} as in the CP-opt procedure.¹² Thus, optimizations on PES's that are not corrected for BSSE can lead to artefactual minima. The foregoing is especially true for weak interactions.

As part of our evaluations of new functionals abilities to correctly describe dispersion interactions, we have reinvestigated this problem using several functionals and compared them to results obtained with high-level ab initio calculations, such as MP2 and CCSD(T), using more complete basis sets than used in the earlier studies. We have identified a third, T-shaped, structure, calculated the vibrational shifts from this, the π -stacked and planar structure previously identified as that of the dimer in the argon matrix (see figure 1).

METHODS

All calculations were performed using the GAUSSIAN 09 suite of computer programs.¹³ Except where explicitly indicated, all structures were optimized with respect to all internal coordinates. Harmonic frequencies were calculated for these optimizations to confirm the existence of a minimum (no imaginary frequencies), to obtain the gas phase enthalpies that correspond to these structures, and to evaluate the vibrational frequency shifts for comparisons with the reported experimental observations. Counterpoise (CP)

corrections^{10,11} were calculated either on the CP-corrected surface¹² or as single point a posteriori calculations or both. When a CP-corrected surface was used, the frequencies were calculated on this surface.¹² We used the frequencies to calculate the ΔH_{int} at 12 K (the temperature of the experiment in the Argon matrix) and to calculate the frequency shifts for comparison with the experimental observations.⁸ We considered the following functionals designed to include dispersion interactions: B97D,¹⁴ ω B97X-D,¹⁵ M05,¹⁶ M05-2X,¹⁷ M06, M06-2X, M06L¹⁸ and the following traditional functionals: B3LYP,^{19,20} PBE1PBE,²¹ X3LYP²² for comparisons with MP2, and CCSD(T) using the D95++** and cc-pVTZ basis sets. The 99974 grid of the GAUSSIAN 09 program was used, as using less stringent criteria gave rise to inconsistent (including imaginary) frequencies with some of the functionals designed to include dispersion interactions. These disappeared when we applied the stricter criteria. We performed single point CCSD(T)/cc-pVTZ calculations at the optimized MP2/cc-pVTZ geometry and used the vibrational analyses from the MP2 calculations to calculate the vibrational corrections to the enthalpy at 12 K.

RESULTS

We could not find any minima for the stacked geometry using B3LYP, X3LYP, or PBE1PBE, which is consistent with Adamowicz's report.⁸ Our attempts to find optimized stacked structures using these functionals led to a T-shaped complex which contains a rather bent H-bond between a C-H of the pyrimidine and one of the O's of the p-benzoquinone, while one of the C-H's of the former interacts with the π -systems of the latter (see figure 1). This structure has not been previously reported. We added this structure to the three others previously reported: stacked, planar A, and planar B, (see figure 1) for our evaluation of the relative energies and enthalpies of the possible dimers.

As seen from tables 1 and 2, the relative ΔE_{int} 's and ΔH_{int} 's depend both upon the method and basis set used. At the highest level for which geometric optimization was performed (MP2/cc-pVTZ), the stacked geometry has both the largest negative ΔE_{int} and ΔH_{int} , followed by T-shaped and planar B. When one considers all the calculations (including those using DFT), the only constant in the trend is that Planar B is always predicted to be more stable than planar A, both in ΔE_{int} and ΔH_{int} . For this reason, we removed Planar A from further consideration. The trends for ΔE_{int} and ΔH_{int} remain mostly the same. Otherwise, the relative stabilities of the structures depend upon the method chosen. Three of the functionals designed for dispersion interactions find an overall minimum for the stacked structure: B97-D, M06-2X and ω B97x-D, two, M06 and M06L predict the T-shaped structure to be more stable, while the other two, M05 and M05-2X correctly find the Planar B structure to be most stable using both basis sets. If we consider which of the three structures (other than planar A) each functional predicts to be the least stable, we see that M06-2X and M06L all predict the planar B structure to be least stable (as does MP2), while B97-D gives similar results for cc-pVTZ, but predicts the T-shaped structure to be least stable with D95++**. ω B97x-D predicts the T-shaped structure to be least stable with both basis sets. M05, M05-2X and M06 all predict the stacked structure to be least stable, while the traditional functionals (B3LYP, X3LYP and PBE1PBE) do not find a minimum for this structure.

Since we find no consistency to these results, and since the MP2 results find the experimentally observed structure to be the least stable of the three, we decided to: 1) recalculate the energies using a more accurate method; and 2) fit the frequency shifts calculated by each method to those of the experimental report.⁸ We recalculated the energies using CCSD(T)/cc-pVTZ at the geometries obtained from the MP2 optimization with this basis set. As seen from tables 1 and 2, the planar B structure now becomes most stable,

while the stacked structure becomes least stable, which is consistent with the report by Sadlej.⁹

The frequencies differ somewhat from those previously reported as those were calculated using HF/6-31++G** on a minimum that was obtained from a mix of different full and partial optimizations without CP-corrections (which was applied a posteriori only to the energies). We calculated frequencies on the CP-corrected surfaces used for optimizations.

We chose to use seven of the frequency shifts reported. We eliminated those reported at 1659 (benzoquinone) and 1570 (pyrimidine) cm^{-1} as these frequencies are coupled to others in the monomers. Table 3 presents the calculated frequency shifts using MP2/cc-pVTZ. We cannot use the MP2/D95++** frequency shifts as the uncomplexed p-benzoquinone has one imaginary frequency at this level of calculation, similar to those previously observed for arenes using MP2 and small basis sets.²³

The frequency shifts for planar B predicted by all methods used best correspond to those found experimentally (see table 4), as previously suggested,⁸ despite the fact that only B3LYP, X3LYP, PBE1PBE (which could not find a minimum corresponding to the stacked dimer), and M05 and M05-2X found this structure to have the lowest enthalpy. The MP2/cc-pVTZ clearly gives the lowest MUE for correspondence with the shifts of planar B. A careful examination of the frequency shifts using MP2/cc-pVTZ in table 3 clearly rules out the stacked dimer from the out-of-plane bending modes for benzoquinone (-5.9 instead of the experimentally observed $+6 \text{ cm}^{-1}$) and pyrimidine (0.5 instead of 3 cm^{-1}), the corresponding calculated shifts for planar B are 6.7 and 4.0 cm^{-1} , much closer to experiment. As noted above, we eliminated the benzoquinone C=O stretches from consideration because they are coupled in the monomer, but not in the adduct. All the calculated shifts for planar B are close to those reported, while the stacked structure actually *predicts shifts in the wrong direction* for four of the seven frequencies useful for assignment. The T-shaped adduct's calculated frequency shifts are intermediate in the quality of the fit to those observed. The major discrepancy is for the band observed at 886 cm^{-1} which is shifted by -6.3 rather than $+6$). In further confirmation, Adamowicz noticed that the pyrimidine band at 1074 and the benzoquinone band at 1060 cm^{-1} become eclipsed in the dimer.⁸ These bands become separated by only 2 cm^{-1} in the planar B, but by 12 cm^{-1} in the stacked structure. One would expect these bands to be readily resolved in the stacked but not the planar B structure.

Table 4 also presents the mean unsigned errors (MUE's) for the assignments of the seven reported band shifts that we considered. One sees from this table that the MUE for the fit of MP2/cc-pVTZ to the experimental frequencies for planar B is quite good, while the fits to the other structures have somewhat larger MUE's. All the functionals, when used with the 99974 grid, have lowest MUE's for the fit to planar B, despite their widely varying predictions for the relative interaction energies and enthalpies. The functionals have somewhat larger MUE's for their fits to planar B than that for MP2/cc-pVTZ. We include MP2/d95++** in the table but note the planar B structure retained the imaginary frequency found for the p-benzoquinone monomer.

DISCUSSION

The current results strongly suggest that several of the dispersion corrected functionals improperly evaluate the relative influences of dispersion and H-bonding (which all methods describe reasonably well). They also confirm that the planar B structure best corresponds to the experimental dimer. However, all methods except CCSD(T)/cc-pVTZ and those obtained with the M05, M05-2X, PBE1PBE, B3LYP and X3LYP functionals predict either

the stacked or T-shaped dimer to be most stable. The various diffusion corrected functionals make rather different predictions. The MP2 results with both moderate (D95++**) and relatively large (cc-pVTZ) basis sets erroneously predict the π -stacked dimer to be the most stable. Can we identify the problem? Let us begin by reiterating that every method used predicts the energies of planar structures A and B in the correct order. Clearly, dispersion is less important for H-bonds than for stacking. In fact, a comparison of calculations on water dimer with experiment and high-level calculations shows that some of those functionals not designed to reproduce dispersion behave extremely well.⁶ The problem appears to lie in the proper estimation of the dispersion interactions. For ab initio calculations that use basis sets that describe nucleo-centric hydrogenlike atomic orbitals, both polarization and dispersion (which is simply electron correlated instantaneous polarization) should yield larger stabilizations as the basis sets increase, as noted above. The observation that the MP2/cc-pVTZ favors the stacked structure by 1.1 kcal/mol more than that of the MP2/D95++** calculation and by 0.7 kcal/mol more than the MP2/aug-cc-pVDZ result reported by Sadlej⁹ is consistent with the foregoing. The single point CCSD(T)/cc-pVTZ calculations predict significantly smaller stabilizations for the stacked and T-shaped interactions, while that for the H-bonded planar B hardly changes from that calculated by MP2 with the same basis.

It is hard to interpret these results without coming to the conclusion that either a problem exists with the experimental results or that MP2 calculations with large basis sets overestimate dispersion, which agrees with published results on the π -stacked benzene dimer,^{24–27} although this does not appear to be generally true for all dispersion stabilized complexes.^{5,28} Let us consider the experiment first. The description of the experimental details suggests that the samples were carefully prepared, the conditions optimized and the spectroscopic measurements carefully performed.⁸ The fact that our calculations of the frequency shifts (using a more accurate theoretical method than used originally) provides a better fit to the experimental report argues in favor of a correct experimental interpretation.

Sadlej's report that, with the aug-cc-pVDZ basis set MP2 predicts a stacked while SAPT predicts the planar B dimer to be more stable,⁹ again suggests that MP2 may overestimate the stabilization due to π -stacking. To independently test this hypothesis, we performed single point CCSD(T)/cc-pVTZ calculations at the geometries previously optimized using MP2/cc-pVTZ for each of the dimeric structures. These calculations predict the planar B structure to be the most stable, even without CP correction (which is generally larger for the stacked geometry). We have included these single point calculations with and without BSSE and with vibrational corrections taken from the MP2/cc-pVTZ calculations in table 2. Similar results have been reported for the interactions of 2-pyridone with various fluorinated benzenes. MP2 calculations overestimate the stabilities of π -stacked complexes and predict them to be more stable than the (experimentally observed) H-bonded dimers for all fluorinated benzenes except hexafluorobenzene.²⁹

The foregoing begs the question of whether π -stacking interaction in biochemical systems might be overestimated, as the theoretical estimates of this interaction generally derive from MP2 calculations or CBS extrapolations (sometimes using CCSD(T)-like terms) as in the case of nucleic acid base-pair stacking.² CBS extrapolations that start with small basis sets have recently been questioned by Sherrill, who showed that some terms actually have the wrong sign with these small basis sets.³⁰ The geometry optimization of large structures (such as peptides) with large basis sets becomes too onerous even using DFT, and essentially impossible using such basis sets with MP2 of CCSD(T) using currently available computers and software.

The possible stabilization of amyloids by π -stacking, which often consist of in-register parallel β -sheets³¹ in which phenylalanine and tryptophane are often found is of

considerable interest. However, the present results do not augur well for reliable quantum mechanical estimations of these interactions. MP2 calculations appear to overestimate similar interactions, while the functionals that we tested do not give consistent results.

We have shown elsewhere that several of the functionals designed to assess dispersion interactions (B97-D, ω B97x-D, M06, M06L and M06-2X) do not properly predict the experimental energetics and/or structures of α -helices and β -sheets comprised of polyalanines, while other functionals such as B3LYP and X3LYP perform reasonably well.⁷ One possible reason for this might be the fact that the interactions in these peptide structures are not purely due to dispersion, but to a combination of induction and dispersion. We have shown elsewhere that the more traditional functionals often perform better in such situations as when coupled with induction, dispersion becomes biased so as to reinforce rather than oppose the inductive interaction.⁵ If this be the case, the need for new functionals that have been specifically parametrized to treat dispersion becomes less evident.

Acknowledgments

The work described was supported by Award Number SC1AG034197 from the National Institute on Aging.

References

- Hobza P, Sponer J. J Am Chem Soc. 2002; 124:11802–11808. [PubMed: 12296748]
- Dabkowska I, Jurecka P, Hobza P. J Chem Phys. 2005; 122:204322. [PubMed: 15945739]
- Acosta-Silva C, Branchadell V, Bertran J, Oliva A. J Phys Chem B. 2010; 114:10217–10227. [PubMed: 20684646]
- Marsili S, Chelli R, Schettino V, Procacci P. Phys Chem Chem Phys. 2008; 10:2673–2685. [PubMed: 18464982]
- Roy D, Marianski M, Maitra N, Dannenberg JJ. 2012 submitted for publication.
- Plumley JA, Dannenberg JJ. J Comput Chem. 2011; 32:1519–27. [PubMed: 21328398]
- Marianski M, Asensio A, Dannenberg JJ. J Chem Phys. 2012; 137 in press.
- McCarthy W, Plokhotnichenko AM, Radchenko ED, Smets J, Smith DMA, Stepanian SG, Adamowicz L. J Phys Chem A. 1997; 101:7208–7216.
- Cybulski H, Sadlej J. J Chem Theory Comput. 2008; 4:892–897.
- Jansen HB, Ros P. Chem Phys Lett. 1969; 3:140–3.
- Boys SF, Bernardi F. Mol Phys. 1970; 19:553.
- Simon S, Duran M, Dannenberg JJ. J Chem Phys. 1996; 105:11024–11031.
- Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, GA.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, HP.; Izmaylov, AF.; Bloino, J.; Zheng, G.; Sonnenberg, JL.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, TJA.; Montgomery, J.; Peralta, JE.; Ogliaro, F.; Bearpark, M.; Heyd, JJ.; Brothers, E.; Kudin, KN.; Staroverov, VN.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, JC.; Iyengar, SS.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, JM.; Klene, M.; Knox, JE.; Cross, JB.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Martin, RL.; Morokuma, K.; Zakrzewski, VG.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Dapprich, S.; Daniels, AD.; Farkas, O.; Foresman, JB.; Ortiz, JV.; Cioslowski, J.; Fox, DJ. Gaussian, Inc; Wallingford CT: 2009.
- Grimme S. J Comput Chem. 2006; 27:1787–1799. [PubMed: 16955487]
- Chai JD, Head-Gordon M. Phys Chem Chem Phys. 2008; 10:6615–6620. [PubMed: 18989472]
- Zhao Y, Schultz NE, Truhlar DG. J Chem Phys. 2005; 123:161103. [PubMed: 16268672]
- Zhao Y, Schultz NE, Truhlar DG. J Chem Theory and Comp. 2006; 2:364–382.
- Zhao Y, Truhlar DG. Acc Chem Res. 2008; 41:157. [PubMed: 18186612]
- Becke AD. J Chem Phys. 1993; 98:5648.

20. Lee C, Yang W, Parr RG. *Phys Rev B*. 1988; 37:785.
21. Adamo C, Barone V. *J Chem Phys*. 1999; 110:6158–6170.
22. Xu X, Goddard WA. *Proc Nat Acad Sci U S A*. 2004; 101:2673–2677.
23. Moran D, Simmonett AC, Leach FE, Allen WD, Schleyer PvR, Schaefer HF. *J Am Chem Soc*. 2006; 128:9342–9343. [PubMed: 16848464]
24. Hobza P, Selzle HL, Schlag EW. *J Phys Chem*. 1996; 100:18790–18794.
25. Tsuzuki S, Uchimaru T, Matsumura K, Mikami M, Tanabe K. *Chem Phys Lett*. 2000; 319:547–554.
26. Sinnokrot MO, Sherrill CD. *J Phys Chem A*. 2006; 110:10656–10668. [PubMed: 16970354]
27. Park YC, Lee JS. *J Phys Chem A*. 2006; 110:5091–5095. [PubMed: 16610829]
28. Klopper W, Luethi HP, Brupbacher T, Bauder A. *J Chem Phys*. 1994; 101:9747–54.
29. Bachorz RA, Bischoff FA, Hofener S, Klopper W, Ottiger P, Leist R, Frey JA, Leutwyler S. *Phys Chem Chem Phys*. 2008; 10:2758–2766. [PubMed: 18464991]
30. Marshall MS, Burns LA, Sherrill CD. *J Chem Phys*. 2011; 135:194102–10. [PubMed: 22112061]
31. Shewmaker F, Ross ED, Tycko R, Wickner RB. *Biochemistry*. 2008; 47:4000–4007. [PubMed: 18324784]

Figure 1.
Dimer structures.

Table 1

CP-OPT Energies of interactions in cc-pVTZ and D95++** basis sets (kcal/mole) the 99974 grid and very tight convergence.

	T-shape	stacked	planar A	planar B
cc-pVTZ				
B3LYP	-1.73		-2.36	-3.09
X3LYP	-2.23		-2.80	-3.56
PBE1PBE	-2.45		-3.01	-3.76
B97-D	-4.75	-5.04	-3.92	-4.67
ω B97x-D	-4.80	-5.46	-4.15	-4.96
M05	-3.25	-1.92	-3.36	-4.15
M05-2X	-4.41	-3.85	-3.66	-4.44
M06	-4.54	-3.78	-3.47	-4.32
M06-2X	-4.80	-5.16	-3.46	-4.26
M06L	-4.84	-4.42	-3.16	-3.95
MP2	-4.92	-6.23	-3.77	-4.54
Single point CCSD(T)/cc-pVTZ at MP2 geometry				
No CP	-5.48	-5.20		-5.77
CP-corrected	-3.88	-3.08		-4.52
D95++**				
B3LYP	-1.97		-2.69	-3.49
X3LYP	-2.48		-3.15	-3.97
PBE1PBE	-2.65		-3.31	-4.11
B97-D	-4.87	-5.06	-4.20	-5.00
ω B97x-D	-4.86	-5.36	-4.34	-5.18
M05	-3.51	-2.08	-3.57	-4.41
M05-2X	-4.52	-3.85	-4.00	-4.87
M06	-4.49	-3.52	-3.47	-4.35
M06-2X	-4.84	-5.00	-3.71	-4.54
M06L	-4.81	-4.35	-3.41	-4.25
MP2	-4.97	-5.38	-4.04	-4.80

Table 2

CP-OPT Enthalpies of interactions at 12K using cc-pVTZ and D95++** basis sets (kcal/mole) using the 99974 grid and very tight convergence. MP2 vibrational corrections applied to CCSD(T) single point calculations.

	T-shape	stacked	planar A	planar B
cc-pVTZ				
B3LYP	-1.40		-1.93	-2.56
X3LYP	-1.88		-2.36	-3.04
PBE1PBE	-2.10		-2.58	-3.25
B97-D	-4.27	-4.58	-3.42	-4.12
ω B97x-D	-4.35	-4.95	-3.63	-4.41
M05	-2.90	-1.64	-2.90	-3.58
M05-2X	-3.95	-3.48	-3.21	-4.18
M06	-4.10	-3.04	-2.99	-3.77
M06-2X	-4.36	-4.73	-3.07	-3.69
M06L	-4.40	-4.00	-2.74	-3.44
MP2	-4.56	-5.90	-3.36	-4.06
Single point CCSD(T)/cc-pVTZ at MP2 geometry				
CP-corrected	-3.52	-2.74		-4.04
D95++**				
B3LYP	-1.61		-2.22	-2.95
X3LYP	-2.09		-2.66	-3.41
PBE1PBE	-2.27		-2.84	-3.57
B97-D	-4.37	-4.57	-3.69	-4.42
ω B97x-D	-4.37	-4.91	-3.83	-4.63
M05	-3.10	-1.79	-3.08	-3.83
M05-2X	-3.97	-3.51	-3.53	-4.32
M06	-4.01	-3.15	-2.98	-3.80
M06-2X	-4.33	-4.55	-3.29	-4.04
M06L	-4.34	-3.94	-3.00	-3.73
MP2	-3.89	-4.42	-3.06	-4.34 ^a

^a has one imaginary frequency.

Table 3

Calculated (MP2/cc-pVTZ) unscaled frequency shifts (cm^{-1}) compared to those reported. Pyrimidine and benzoquinone monomers noted by 'p' and 'q'. Frequencies noted from experiment.⁸

	T-shaped	Stacked	Planar B	Experiment
1400 p	1.4	-3.1	7.7	5.0
1301 q	3.7	7.3	4.6	4.0
1223 p	0.7	-0.5	4.3	4.0
886 q	-6.3	-5.9	6.7	6.0
719 p	0.6	0.5	4.0	3.0
621 p	2.4	-1.2	1.9	1.0
407 q	2.9	0.5	2.6	2.0

Table 4

Mean unsigned errors (MUE) for the assignment of the frequency shifts calculated using different methods to the observed shifts.

	d95++**			cc-pVTZ		
	T-shape	Stacked	planar B	T-shape	Stacked	planar B
MP2 ^d	2.7	3.5		3.5	4.4	1.0
B3LYP	2.2		1.4	2.7		1.6
X3LYP	2.2		1.6	2.6		1.6
PBE1PBE	2.5		1.5	2.9		1.4
B97-D	2.8	2.9	1.6	2.7	3.0	1.8
ωB97x-D	2.4	2.9	1.8	2.7	3.0	2.1
M05	2.7	2.7	1.6	2.7	2.8	1.9
M05-2X	2.7	3.1	1.6	3.0	3.1	1.9
M06	3.6	3.9	1.7	3.5	3.5	2.2
M06-2X	2.9	3.2	1.5	3.3	3.7	2.7
M06L	3.9	3.8	1.7	4.3	3.5	2.1
HF/6-31++G**						
Adamowicz (ref. 6)		2.6	1.1			

^d Planar B has one imaginary frequency with d95++**.