Molecular Orbital Study of Crystalline *p*-Benzoquinone

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The interaction energies for the crystal of *p*-benzoquinone and aggregates from two to seven molecules have been calculated using Hartree−Fock and density functional theory methods with different basis sets at the experimental (crystallographic) geometries. After correction for basis set superposition error, all methods predict similar interaction energies. Periodic calculations using CRYSTAL92 and CRYSTAL 95 at the HF/6-21G** level produced values of −5.30 kcal/mol for the interaction energy of a two-dimensional slab. The calculation of the crystalline interaction energy is hampered by the inability of HF calculations to reproduce stacking interactions and the large basis set superposition errors associated with the HF/6-21G** molecular orbital method. The cooperative contributions to the interaction energies calculated for the aggregates imply that roughly half the crystalline interaction energy is due to cooperativity.

Several studies have shown that C−H hydrogen bonds can be extremely important in solid-state interactions.[2] These interactions probably play important (if less apparent) roles in other systems. Crystalline *p*-benzoquinone provides a striking and unusual example of these interactions. *p*-Benzoquinone forms stable crystals with a melting point of 116 °C. A plane from the crystal structure is shown in Figure 1. One clearly sees that all stabilizing interactions between nearest neighbors within a plane are C−H···O hydrogen bonds.

We have previously studied C−H hydrogen bonds between the individual molecules,[3] as well as in crystals,[4] using ab initio molecular orbital techniques. In this study, we apply similar techniques to *p*-benzoquinone in order to understand the nature and the strength of the individual hydrogen bonds involved in the intermolecular interactions leading to crystal formation, as well as their cooperative effects.

Methods

We performed ab initio calculations using the GAUSSIAN 94[5] and both CRYSTAL 92[6] and CRYSTAL 95 (CRYSTAL) suites of programs. CRYSTAL can be used to perform infinite periodic structures in three (crystals), two (slabs), one (polymers), or zero (molecules) dimensions. The periodic nature[7] of the calculations dictate certain approximations, as well as certain basis sets. We chose the 6-21G** basis set as it is also a standard GAUSSIAN 94 basis set and similar to the 6-31G** basis set generally used. The 6-21G** basis is preferred over the 6-31G** for CRYSTAL calculations because diffuse primitive Gaussian functions[8] can lead to SCF conversion problems in the periodic calculations.[9] It has also been reported that the 6-31G** basis set can lead to pseudolinear dependence problems.[10] The tolerance levels were set to the "very good" level. This corresponds to Coulomb overlap, Coulomb penetration, and exchange overlap tolerances of 10^{-6}, 10^{-8}, and 10^{-6}, respectively. Other tolerances refer to pseudo potentials which are not used for atomic numbers through 10. Convergence criteria were 10^{-5} on eigenvalues and 10^{-6} on total energy. We found these values for tolerances and convergence to be necessary to make the CRYSTAL calculations consistent with GAUSSIAN 94 calculations on identical clusters. We changed the conversion factor between Ångstroms and bohrs in CRYSTAL 92 (where it is given to five places) to the more precise value used in GAUSSIAN 94. Without this change there were slight (about 0.6 kcal/mol) differences in the internuclear repulsions for acetic acid monomer.[11] GAUSSIAN 94 uses six d-functions as the default for the polarization functions, while CRYSTAL uses only five. The 6-21G** calculations performed with GAUSSIAN 94 used the (nondefault) value of five d-orbitals.

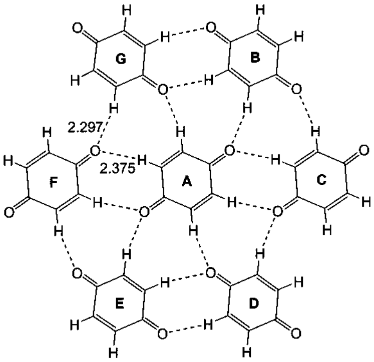

Figure 1. Seven molecules within a plane taken from the experimental crystal structure of *p*-benzoquinone.

We used GAUSSIAN 94 to calculate aggregates of from one to seven *p*-benzoquinone molecules. Both Hartree−Fock (HF) and density functional theory (DFT) were used with the 6-21G** and D95* basis sets. The DFT calculations used the B3LYP and B3PW91 functionals. The B3PW91 method combines Becke's 3-parameter functional,[12] with the nonlocal correlation provided by the Perdew-Wang expression,[13] while the B3PLYP combines the same Becke functional with correlation functional of Lee, Yang, and Parr.[14] In addition, we used the AM1 semiempirical method,[15] which we have shown to give good results for H-bonds other than those involving O−H···O.[16] MP2 calculations of two stacking interactions were also performed. These were limited to dimers.

We prefer to use the results of neutron diffraction studies as input to our calculations, because these directly provide the positions of the hydrogen atoms. However, no neutron diffraction studies of *p*-benzoquinone crystals have been reported. The

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TABLE 1: Energies of Aggregates Calculated Using GAUSSIAN 94 (kcal/mol): See Text for Explanations

			HF			D95*		
M[a]	HB[b]	type[c]	AM1	6-21G**5D	D95*	B3LYP	B3PW91	MP2
			Energy of Interaction					
2	2	AC	−3.01	−3.03	−3.40	−3.49	−2.65	
	1	AB	−1.06	−0.71	−0.79	−0.97	−0.38	
	0	A′A						−0.73
	0	A′D						−1.62
	0	BE	0.03	0.04	0.06	0.04	0.04	
3	4	ACF	−6.07	−6.19	−6.90	−7.03	−5.36	
	2	ABE	−2.06	−1.27	−1.45	−1.89	−0.74	
	2	ADG	−2.03	−1.17	−1.36	−1.82	−0.67	
	4	ABC	−5.18	−4.61	−5.01	−5.56	−3.60	
4	7	ABCG	−9.31	−8.49	−9.18	−10.00	−6.71	
	6	ABCD	−7.54	−6.65	−7.08	−8.13	−5.04	
7	16	ABCDEFG	−21.16	−19.51	−20.85	−23.23	−15.48	
			Total Cooperative Interaction					
2	2	AC	−0.88	−1.61	−1.82	−1.55	−1.89	
	1	AB	0.00	0.00	0.00	0.00	0.00	
3	4	ACF	−1.81	−3.35	−3.73	−3.15	−3.84	
	2	ABE	0.07	0.15	0.13	0.05	0.02	
	2	ADG	0.09	0.25	0.22	0.12	0.09	
	4	ABC	−0.93	−1.77	−1.84	−1.68	−2.08	
4	7	ABCG	−1.86	−3.52	−3.63	−3.21	−4.05	
	6	ABCD	−1.16	−2.39	−2.33	−2.31	−2.76	
7	16	ABCDEFG	−4.14	−8.15	−8.16	−7.71	−9.40	
			Estimate of Infinite Sheet Energy from Aggregate					
total			−5.44	−5.30	−5.44	−6.19	−4.33	
cooperative component			−1.19	−2.46	−2.26	−2.31	−2.81	

[a] Number of molecules in aggregate. [b] Number of H-bonds in aggregate. [c] See Figure 1 for key.

present calculations use the experimental crystal geometry taken from the X-ray diffraction study of Van Bolhuis and Kiers,[17] performed at -160 °C ($r = 0.074$). An earlier X-ray diffraction study at room-temperature had been reported.[18] The coordinates were taken directly from the Cambridge Crystallographic Data Base.[19] The positions of the H-atoms were fixed at 1.08 Å from the carbon atoms in the crystal structure. *p*-Benzoquinone crystallizes with a unit cell containing two molecules in space group $P2_1/a$. Both molecules of the unit cell provided the repeating unit for the three-dimensional (crystal) and two-dimensional (slab) calculations. One molecule is sufficient for the repeating unit in one of the one-dimensional chains, while two molecules are necessary for the other two (equivalent) chains. One should note that the H-bonding sheets in the crystal slightly deviate from planarity.

The counterpoise[20] corrections to the basis set superposition error were performed differently in the aggregate and periodic calculations. This correction is somewhat controversial.[21] For the aggregates, the counterpoise (CP) correction was evaluated from the calculation of each monomeric unit in the presence of the ghosts of all the others. In the periodic calculations, the counterpoise correction was calculated using the ghosts of all atoms located closer than 4 Å to any atom of the monomeric unit. The distance was chosen as a compromise between disk space and precision. CP correction is particularly large for the 6-21G** (5D) basis set used in the CRYSTAL calculations. However, after correction the interaction energies of the clusters for this basis that became approximately equal to those calculated using the other methods.

No geometric optimizations were attempted for these reasons: (a) We wish to evaluate the interactions at the experimental geometries and (b) large basis set superposition errors (BSSE) and consequent counterpoise corrections would be expected to adversely affect the reliability of the potential energy surface.[22]

The AM1[15] semiempirical method was used to calculate the aggregates for comparison. This method has been shown to give accurate results for C−H···O interactions in dimeric H-bonding interactions[23] and reasonable (no energetic comparisons for these specific interactions are available) results in aggregate calculations.[24]

Results and Discussion

Cluster Calculations. The interaction energies for clusters containing up to seven benzoquinone molecules calculated five different ways are collected in Table 1. For simplicity of discussion, where individual energies are cited in the following discussion, we shall use the B3LYP/D95* calculated values. These seem most appropriate since they are in reasonable agreement with three of the other methods, while the B3PW91 results seem to differ. Only the B3LYP, B3PW91, and MP2 methods allow for electron correlation.

The energy of an individual hydrogen bond was taken as that of the AB dimer (see Figure 1), because this is the only dimer that contains only one hydrogen bond. The stabilization energy of 0.97 kcal/mol is consistent with other calculations on C−H···O interactions of this type. The results of the calculations on the AC dimer and other aggregates suggest that H-bond cooperativity plays an important role in the crystal interaction energy. We approximated the cooperativity of each aggregate calculated using GAUSSIAN 94 by subtracting the appropriate number of individual hydrogen bond energies from the total interaction energy. Within the planar structure depicted in Figure 1, one can trace several kinds of cyclic hydrogen-bonding interactions. One kind of ring involves two molecules, each providing a hydrogen bonding donor and an acceptor. Molecules A and C form such a cycle. These hydrogen bonding rings contain eight atoms and six π-electrons in a ring and provide the proper polarization (alternating positive and negative) in the σ-system. A second kind of ring involves three molecules.

TABLE 2: Periodic Calculations Using CRYSTAL at the HF/6-21G Level: Aggregate Calculations Using Trimers in Place of Infinite Chains with the Same Basis Set Are Included for Comparison**

	periodic calculation			aggregate calculation	
chains	uncorrected	CP-corrected	using MP2/D95* dimeric A′D and A′A	uncorrected	CP-corrected
ACF	−8.71	−3.35		−8.73	−3.35
ABE	−3.13	−0.85		−1.20[a]	−0.20[a]
ACF + 2 ABE	−14.97	−5.05		−10.13	−3.75
slab	−15.20	−5.49		−15.49	−5.30
stack A′D	−0.34	+1.78	−1.62		
stack A′A	−0.64	+0.18	−0.73		
all chains	−16.28	−1.31			
crystal	−15.17	−0.93	−9.46[b]		

[a] The average of ABE and ADG from Table 1. [b] The MP2/D95** values for the dimers replace the two stack A′D and stack A′A periodic HF calculations and are added to the corrected slab interaction.

Molecules A, B, and C form such a ring. Here, one molecule, A, provides two acceptors, the second molecule, B, provides a donor and an acceptor and the third molecule, C, provides two donors within the H-bonding ring. These H-bonding rings also contain 6 π-electrons, but do not provide the proper polarization (alternating positive and negative) in the σ-system as they contain and odd number (nine) of atoms. Consequently, the AC ring leads to a much larger cooperative interaction than the ABC ring. Each aggregate composed of three or more molecules that contain an ABC ring must also contain at least one AC type ring. The cooperativity due to the ABC ring can be estimated as the difference between the total cooperativity in ABC, less the cooperativity of the AC ring. The data in Table 1 indicate the ABC ring cooperativity (−0.13 kcal/mol) to be about 10% of the AC cooperativity (−1.55 kcal/mol). Inspection of Figure 1 leads to identification of larger H-bonding rings (each of which contains one or more smaller ones).

One can identify H-bonding rings, including those that traverse many molecules, which contain the aromatic quantity, $4N + 2$ π-electrons. For example, one can identify H-bonding rings that traverse molecules B, C, D, E, F, and G. These H-bonding rings contain from 32 to 38 atoms and 22, 24, and 26 π-electrons. Both 22 and 26 correspond to $4n+2$, while 24 does not. However, the 24 electron route traverses the same molecules as the 22 and 26 electron routes. Previous theoretical calculations on the enol of acetylacetone have suggested that aromaticity might play a role in the stability of cyclic H-bonding systems.[25] In that system, (which, also, contains the proper charge alternation to polarize the six atoms in the H-bonding ring optimally) the internal hydrogen bond was found to be 12 kcal/mol, half of which is due to cooperativity (or aromaticity). For comparison, the cooperativity of the AC ring is also roughly half (1.55 kcal/mol) the total stabilization (3.49 kcal/mol).

Aside from the ABC aggregate discussed above, two other trimeric aggregates are identifiable from Figure 1: ACF and ABE. ACF contains two AC interactions. The central molecule, A, is polarized oppositely by its two partners, C and F. As a result, the additional cooperativity in the ACF aggregate (as compared to two AC's) is negligible (−0.05 kcal/mol). One should note that each hydrogen bonding ring involving all three molecules contains $4n+2$ (10, 14, or 18) π-electrons. The ABE aggregate is destabilized slightly (+0.05 kcal/mol) relative to two AB interactions. The likely cause is a repulsive interaction of 0.04 kcal/mol (Table 1) between molecules B and E (due to their relative orientations) combined with the uncooperative polarization of the central molecule, A. Since there are no cyclic H-bonding structures in ABE, no aromatic stabilization is possible.

The total cooperative contribution to the seven-molecule aggregate (−7.71 kcal/mol) is roughly one-third the total interaction energy (−23.23 kcal/mol), about 10% more than would be expected from adding the cooperative contributions from each of the interactions (−6.98 kcal/mol). We estimate the stabilization energy of an individual molecule in an infinite sheet from the heptamer (−6.19 kcal/mol) by subtracting the stabilization due to the eight H-bonds (two AC rings and four H-bonds) that do not involve the central molecule, then dividing by two (as each hydrogen bond involves two molecules). The cooperative contribution is 37% (−2.31 kcal/mol).

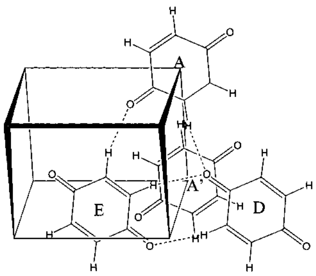

Figure 2. Four molecules from the experimental crystal structure of *p*-benzoquinone. Molecules A, D, and E correspond to the same molecules in Figure 1. Molecule A′ corresponds to a molecule equivalent to A in a plane behind that of A, D, and E.

Periodic Calculations. The results of periodic calculations on infinite chains, slabs, and the three-dimensional crystal are collected in Table 2. Due to limitations in the CRYSTAL programs, we were constrained to work at the HF/6−21** level, using five d-orbitals (rather than the six used in the more common Gaussian basis sets). Individual (finite) aggregates were calculated using this procedure for comparison with the periodic calculations. In the following discussion, all energies (including the cluster calculations that are used for comparison) refer to values obtained using this procedure. These large CP corrections required to offset the BSSEs have complicated the analysis of these calculations. In many cases, the CP correction accounts for more than half the (uncorrected) interaction energy. The fact that the CP corrections are so large combined with the substantially different procedures necessary for calculating CP in CRYSTAL makes comparisons somewhat difficult.

The CRYSTAL calculations are summarized in Table 2. In the crystal structure, one can identify four different types of chains formed by the nearest neighbors in the benzoquinone crystal: two within the planar sheet (formed by molecular contacts of AB and AC type), and two involving molecules in adjacent sheets (stacking interactions). The different stacking interactions involve interactions of the type A′D (energetically equivalent to A′E) and A′A (see Figure 2). The stabilization/molecule of infinite chain AC before CP correction shows no additional cooperative effect beyond the stabilization of the dimer (8.7 kcal/mol for both), but roughly 10% additional cooperativity after CP correction (3.3 vs 3.0 kcal/mol). This result is consistent with the small additional cooperativity (over two AC's) of the ACF aggregate discussed above. The interaction energy per hydrogen bond of chain AB is less than for the dimer (−3.1 vs −3.3 kcal/mol) before CP correction. This appears to be consistent with the calculation of the ABE aggregate (discussed above), where the interaction was slightly less than that of two ABs. However, unlike the BE interaction which is repulsive, the CF interaction should be attractive. The chains that involve stacking interactions, A′D and A′A, have interactions energies of −0.34 and −0.64 kcal/mol, respectively. However, they both become repulsive after CP correction (see Table 2). The sum of interaction energies over in-plane chains (taking into account that each molecule participates in one AC and two AB chains) is −15.0 kcal/mol before CP correction to be compared to −15.2 kcal/mol interaction energy/mol of the infinite sheet. Nonadditivity of the CP correction makes BSSE corrected values difficult to compare. The sum over all chains leads to the total stabilization of 16.28 kcal/mol vs 15.20 kcal/mol for the 3D structure. The apparent negative cooperative effect could be due to repulsive 1−3 interactions between molecules in different chains as well as the nonadditivity of the BSSE.

Stabilization of the double infinite sheet is 15.20 before and 5.49 kcal/mol after CP correction, as calculated by this method. Thus, the sheets have no interaction before CP correction, but repel each other by 3.74 kcal/mol after correction. The crystal stabilization after CP correction (0.9 kcal/mol) is consistent with the facts that each sheet has two neighbors in 3D structure and that there should be a repulsive interaction between every second sheet. The repulsion between adjacent sheets must clearly be an artifact of the calculation. There are several reasons for this repulsion: (1) the intermolecular distances are not optimized for this basis set and fell into repulsive region of the potential curve; (2) the basis set gives large BSSE; (3) the HF method systematically underestimates dispersion energy, which is important for $\pi-\pi$ stacking interactions. MP2/D95* calculations give stacking interactions between sheets that are attractive by 3.97 kcal/mol (two A′D interactions of −1.62 and one A′A interactions 0f −0.73 kcal/mol). If this stacking interaction is used to replace the 3.74 kcal/repulsion, the crystal interaction becomes −9.46, instead of −0.93 kcal/mol. In any case we can conclude that stacking interaction between the sheets in the crystal are weaker then the H-bonding interactions. This is consistent with a weak stacking energy. A recent report shows that the stacking interaction is less stabilizing than the H-bonding dimer interaction for the *p*-benzoquinone/pyridine dimer.[26] HF interaction energies are generally smaller than similar interactions calculated using methods that account for electron correlation. This effect occurs for both H-bonds and stacking interactions. In principle, the stacking interaction between two nonpolar molecules might be close to zero for HF calculations.[27] Interactions that are often attributed to dispersion forces or time-dependent polarization are poorly treated by HF calculations. The DFT methods used here provide interaction energies for H-bonding systems that are as good or better than second-order Møller−Plesset (MP2) calculations for the water dimer.[28,29,30] However, a recent report indicated that there was no stability to stacking of benzoquinone and pyridine when calculated either by HF or DFT methods.[25] MP2 calculations overestimated the stability of the stacking interactions. Only after BSSE correction of the MP2 calculations did the (experimentally observed) planar H-bonding interactions become more stable than the stacking interactions. The best stacking interaction (before vibrational correction) for benzoquinone/pyridine was reported to be 3.06 kcal/mol, or about twice the apparent stacking in benzoquinone crystals as estimated above.[25] While electron-correlation is accounted for in DFT methods, these methods have not been successful for calculating dispersion interactions.[31]

The experimental heat of sublimation for benzoquinone has been reported as 15.0 ± 0.8 kcal/mol.[32] This value, while close to the uncorrected three-dimensional periodic value calculated by CRYSTAL, is about 1.5 than the most reasonable (corrected) calculated interaction energies even if one replaces the repulsive stacking interactions with the attractive MP2/D95** values for the A′D and A′A dimers (which leads to a crystal energy of 9.46 kcal/mol). If one estimates the stacking interaction to be about 3 kcal/mol from benzoquinone/pyridine stacking value, the calculated sublimation energy for benzoquinone becomes about 8.5 kcal/mol, a slightly lower value. One might assume that this value might become somewhat greater if one used the B3PLYP procedure instead of HF/6-21G**. The B3LYP calculation of the stabilization in the seven molecule aggregate is 17% greater than that calculated by HF/6-21G** for the same system. Applying this correction to the CRYSTAL slab calculation and using the MP2/D95** values for the stacking stabilization would yield an estimate of 10.4 kcal/mol for the heat of sublimation. These calculated interactions do not include vibrational corrections, relaxation of the geometry of the crystal to that of the monomer or the PΔV work done upon sublimation.

The AM1 calculations, that were performed for comparison, give results for the individual interactions that are similar to the ab initio aggregate values, although the cooperative components are some what lower. These results suggest that AM1 could be useful for calculations on large aggregates that are too complex for accurate ab initio calculations.

Conclusions

Calculations using various ab initio an semiempirical methods give similar results for the hydrogen bonds within aggregates containing up to seven *p*-benzoquinone molecules taken from the experimental crystal structure.

The disaccord between the experimental and theoretical results might be due to one or more of several factors. (1) The experimental X-ray structure used as a basis for these calculations did not explicitly locate the hydrogen atoms. If the C−H distances are underestimated, the H···O distances will, consequently, be overestimated. This would lower the calculated hydrogen bond stabilization. (2) The cooperative component of the crystal interactions might be poorly approximated by the CRYSTAL calculations. (3) The estimate of the stacking interaction or its cooperativity might be inadequate. To the extent that MP2 calculations on the dimer are used, no cooperativity is taken into account. (4) There may be errors in the experimentally determined heat of sublimation. Nevertheless, the individual C−H···O hydrogen bonding energies are in reasonable accord with those previously reported for other systems.

Cooperativity accounts for approximately half the interaction energy of the seven molecule aggregate. Since the capacity for cooperativity will be greater in the infinite three-dimensional crystal, the cooperative component of the crystal lattice energy must be somewhat greater than that calculated for this aggregate.

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