Acknowledgment. We thank Dr. M. D. Ward for electrochemical studies, Dr. R. L. Harlow for X-ray analysis, Dr. R. H. Staley for infrared studies, and Dr. S. D. Ittel for a gift of $Ti(toluene)_2$.

Supplementary Material Available: Detailed preparation of $[Ti(OC_6H_4O)_2]_n$, TGA curve of $[Ti(OC_6H_4O)_2]_n$, and infrared spectral data on products from reaction of $Ti(NMe_2)_4$ with 4,4′-isopropylidenediphenol and with 4,4′-diphenol, from reaction of $Cr(benzene)_2$ with *p*-benzoquinone, from reaction of $Zr(NEt_2)_4$ with 1,4-hydroquinone, and from reaction of $Ti(tol)_2$ with 1,4-anthraquinone and with 2,5-dihydroxy-1,4-benzoquinone (3 pages). Ordering information is given on any current masthead page.

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AM1 Study of Hydrogen-Bonded Mixed Dimers of Substituted Benzoic Acids

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Received August 9, 1990

Crystals of stoichiometric 1:1 mixtures of compounds that can complex with each other have been shown to form preferentially, rather than pure crystals of the individual components. In some cases these crystals have potential nonlinear optical properties. An interesting example is the 1:1 mixture of *p*-aminobenzoic acid and *m*,*m*-dinitrobenzoic acid.[1] A view of the crystal structure is shown in Figure 1. Examination of this figure leads one to the hypotheses that the preference for the mixed crystal may be due to either (a) a more stable H-bonded interaction between the different benzoic acids in the heterodimer than in the homodimer or (b) the ability of the mixed crystal (heterodimers) to H bond between their amino and nitro groups. It is likely that both of these factors play a role in the stability of the crystal structure. Calculational modeling can aid in determining the importance of these factors.

To determine whether molecular orbital methods could be used to predict and explain preferences for cocrystallization analogous to that discussed above, we present AM1 calculations on the dimerization energies of variously substituted benzoic acids.

Methods

The AM1[2] approximation to molecular orbital theory has been used for these studies. This method overcomes the problems that previous semiempirical methods (notably, MNDO[3]) have in describing hydrogen bonds. It has been used with success in several hydrogen-bonding studies,[4] including modeling of the H bonding between molecules of various nitroanilines in the crystalline state.[5] Ab initio studies of H-bonding systems are very sensitive to basis set and correction for electron correlation, as exemplified in studies of the water dimer.[4b,6] Calculations of sufficient accuracy on molecular complexes of the size to be considered here are not practicable using such costly methods.

All geometrical parameters for each monomer and dimer were individually optimized.

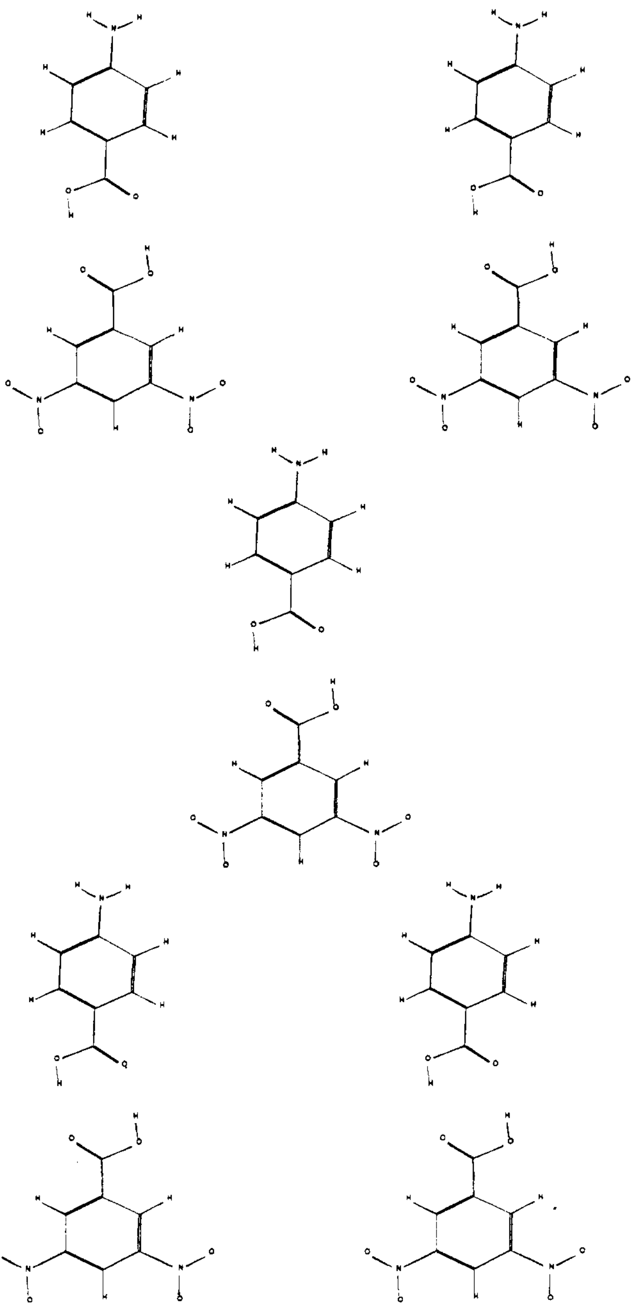

Figure 1. H-bonded aggregate of the crystal of the 1:1 complex of *p*-aminobenzoic acid and 3,5-dinitrobenzoic acid.

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Table I. AM1 Calculated H-Bonding Interactions for Homo- and Heterodimers of Substituted Benzoic Acids (kcal/mol)

monomer A	monomer B	$-H_{\text{interaction}}$
p-nitro	*p*-nitro	6.1
p-amino	*p*-amino	6.1
3,5-dinitro	3,5-dinitro	6.1
3,5-diamino	3,5-diamino	6.3
p-nitro	*p*-amino	6.5
p-nitro	3,5-dinitro	6.7
p-nitro	3,5-diamino	6.6
p-amino	3,5-dinitro	7.2
p-amino	3,5-diamino	6.1
3,5-dinitro	3,5-diamino	7.0

Results and Discussion

In this study we considered all possible dimers between *p*-amino-, *p*-nitro-, *m,m*-diamino-, and *m,m*-dinitrobenzoic acids. The results are indicated in Table I. It is immediately apparent that the heterodimers are generally more stable than the homodimers. Coincidentally, the *m,m*-dinitrobenzoic acid–*p*-aminobenzoic acid dimer (reported by Etter[1]) is the most stable of the group. The implication of the data is that the H bonding within the dimer seems to be of some importance. The accuracy of this prediction was tested by mixing *m,m*-dinitrobenzoic acid with (dimethylamino)benzoic acid to see if a 1:1 crystalline material formed. In this case, H bonding between the nitro and amino groups is precluded by the methylation of the amino groups. Apparently, a stoichiometric mixed solid does form (as evidenced by an unmistakable change in color to red), although the structure has not yet been determined.[7]

In a previous study of hydrogen-bonded dimers of various nitroanilines, we reported that the charge alternation of the individual monomer units was accentuated in each of the monomer units of the dimer.[5] In contrast the local charges on the carbons of the aromatic rings of the various benzoic acids are virtually unchanged upon hydrogen bonding. The foregoing is true irrespective of the substituent groups on the benzoic acids, even when one bears nitro and the other amino groups. One is tempted to note that since there are six π-electrons in the cyclic H-bonding structure formed by a nitro and an amino group, while eight in that formed by two carboxylic acids, aromaticity might be involved. Aromaticity has been discussed with reference to the internal H bonds of the enols of β-dicarbonyl compounds.[8,9] While this concept bears further investigation, the orbitals in neither case seem to support aromaticity. In particular, orbitals that are delocalized over the two H-bonding entities may have nodes between them but not through them.

The H-bonding energies presented here are somewhat lower than those expected from the reported H-bonding energies of gas-phase carboxylic acids. Notably, those reported for formic and acetic acid are roughly twice the calculated values.[10] The AM1 values for the interactions of two formic and acetic acid molecules (6.4 and 6.5 kcal/mol, respectively) are similar to those of the benzoic acids. Previously reported ab initio (STO-3G, DZ, DZ+P) calculations have determined H-bonding energies for the dimers of formic[11,12] and acetic[13] acids close to the accepted experimental gas-phase values.

It seems apparent that the AM1 calculations underestimate the H bonding in the acid dimers. This may be due to a continued slight overestimation of H–H repulsion energies (as in MNDO). One should note that in the carboxylic acid dimers, the two H's from *different* molecules approach each other in the dimer. Perhaps the repulsion between these H's (as calculated by AM1) destabilizes the dimer. This point is illustrated by the fact that AM1 predicts the O–H- -O distance in formic acid dimer to be 3.06 Å compared to the experimental value of 2.73 Å.[10] Ab initio optimizations predict 2.54 (STO-3G),[11,12,14] 2.705 (4-31G),[15] 2.700 (DZ),[12] and 2.779 Å (DZ+P).[12] The carboxylic H's are 2.95 Å apart in the AM1 optimized geometry. The longer O–H- -O distance in AM1 is consistent with the hypothesis that the differential H- -H repulsions are responsible for the low binding energy predicted. For the nitroanilines, and other cases studied, the two H's that are close in the dimer are on the same monomeric unit; therefore, this repulsion does not contribute to the interaction energy. Despite the observation that the AM1 interaction energies are too low for the carboxylic acid dimers, it remains apparent that the relative interaction energies can be useful in predicting the likelihood of 1:1 stoichiometrical cocrystallization of the substituted benzoic acids.

Conclusion

In conclusion, AM1 calculations seem to be a useful tool for estimating the intermolecular interactions that determine whether or not cocrystals will form in preference to crystals of the individual components of a mixture. For the case of substituted benzoic acid, very small energy differences in the H-bonding dimerization energy (~1 kcal/mol) are sufficient to determine which crystal structure will form.

Acknowledgment. This work was supported in part by a PSC-BHE grant.

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Chemical Vapor Deposition of Copper from Copper(I) Trimethylphosphine Compounds

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Received February 2, 1990

Chemical vapor deposition (CVD) of metals from metal organic precursor compounds has been the subject of much

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0897-4756/90/2802-0636$02.50/0