

An AM1 Molecular Orbital Study of Hydrogen Bonding in Crystalline Nitroanilines

L. K. Vinson and J. J. Dannenberg*

Contribution from the Department of Chemistry, City University of New York, Hunter College and The Graduate School, 695 Park Avenue, New York, New York 10021.

Received June 6, 1988

Abstract: The intermolecular interactions between pairs of six different nitroanilines have been investigated using the AM1 molecular orbital method. This method is shown to be quite useful for analyzing and understanding the interactions that give rise to the observed crystal lattices. The optimized geometries of the individual units in the dimers differ from those obtained for the same monomeric molecules. These results imply that molecular orbital methodology applied to small molecular aggregates (such as dimers) may be useful for the investigation of the differences between the geometries of molecules in the gas and solid phases.

Until recently, molecular orbital theory has been unsatisfactory in its predictions of hydrogen bonding in any but very small systems. Only very large basis set *ab initio* calculations are successful in calculating hydrogen bonds. However,¹ these methods are very costly and time consuming. The AM1 molecular orbital method,² a modification of the MNDO method, is the only effective, general semiempirical method for the calculation of hydrogen bonding.

Etter et al.³ have analyzed crystal structures of 28 nitroanilines and 13 related compounds. The primary determinants in the packing patterns of nitroanilines are thought to be the intermolecular hydrogen bonds between aniline donors and nitro acceptors. Many of these structures involve bifurcated hydrogen bonds. To investigate this hypothesis, we have chosen to model the interaction of dimers of six of the compounds [*p*-nitroaniline (I), *o*-nitroaniline (II), *m*-nitroaniline (III), *N*-methyl-*p*-nitroaniline (IV), *p*-nitro-*o*-toluidine (V), and 2,6-dinitroaniline (VI)] considered by Etter, using molecular orbital methods. In particular, we compare the optimum H-bonding dimers with the crystal structure in order to better understand how the former influence the latter.

Methods

The AM1 approximation to molecular orbital theory has been used for these studies. This method overcomes the problems that previous semiempirical methods (notably, MNDO⁴) have in describing hydrogen bonds. It has been used with success in several hydrogen-bonding studies.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. 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 of the monomers were optimized. For the dimers, all of the geometrical parameters for the second monomer unit were set equal to those of the first except for the parameters (bond lengths, angles, and dihedral angles) of the amino hydrogens and the nitro oxygens directly involved in the intermolecular hydrogen bonds. In order to better approximate the crystal environment, the aromatic rings of the two monomer units were constrained to be coplanar.

Three general dimer types were considered for each of the nitroanilines I-VI: (A) the optimal dimer with two distinct H-bonds, each between one amino hydrogen and one nitro oxygen as the constraints; (B) a

relaxed geometry, with at least one bifurcated H-bond that is, the local minimum closest to the crystal structure; and, (C) the structure obtained by fixing the H-bonds at their experimental (crystal structure) distances and optimizing the rest of the dimer within the same constraints as A and B. Structure C is closest to the experimental structure.

Results

The geometries of the three different nitroaniline interactions for each of the six species studied are presented in Figures 1-6. For *p*-nitroaniline (I), the optimal interaction (IA) has two distinct H-bonds, one between each amino hydrogen and a corresponding oxygen on the nitro group of the other monomer. The hydrogen H-bonding distances are 2.25 Å each. The relaxed structure (IB) has bifurcated interactions between one of the amino hydrogens and both of the nitro oxygens. Hydrogen-bond distances are 2.29 and 2.31 Å. Additionally, one of the nitro oxygens is 2.47 Å from an ortho hydrogen of the ring. The crystal structure (IC) resembles structure B. The bifurcated bond is now unsymmetrical with distances being 2.34 and 3.22 Å, while the ortho bond distance shortens to 2.03 Å (see Figure 1).

The interactions for the *o*-nitroaniline (II) dimer are very similar to those for I. For IIA, the hydrogen-bond distances are slightly longer, 2.23 and 2.33 Å, respectively. Structure IIB is also bifurcated and again includes a hydrogen bond to the ortho hydrogen. Structure IIC again resembles IC except the hydrogen bond to the ortho substituent is longer, 2.34 Å (see Figure 2).

The *m*-nitroaniline (III) dimer differs from the *o*- and *p*-nitroanilines. Although the optimal interaction (IIIA) again contains two distinct H-bonds, and the relaxed structure (IIIB) has a bifurcated structure involving an H-bond to an ortho hydrogen, the crystal structure has no interaction between a nitro oxygen and an ortho hydrogen. Instead, one amino hydrogen H-bonds with both oxygens on the other monomer, 2.30 and 2.55 Å, and one of the oxygens H-bonds with both hydrogens of the amino group (see Figure 3).

In the case of the *N*-methyl-*p*-nitroaniline (IV) dimer, there is only one amino hydrogen available to H-bond. A structure similar to IA with two distinct H-bonds is not possible. The optimal interaction is, therefore, the bifurcated structure IVB. The amino hydrogen is 2.23 and 2.50 Å, respectively, from the nitro oxygens while a nitro oxygen is 2.39 Å from an ortho hydrogen. The crystal structure is similar except the other nitro oxygen is now 2.87 Å from a methyl hydrogen (see Figure 4).

For the *p*-nitro-*o*-toluidine (V) dimer, where the ortho substituent to the amino group is a methyl group, the optimal interaction has two distinct H-bonds as in IA. The hydrogen-bond distances are almost identical with those of IA, 2.21 and 2.29 Å. In the bifurcated structure VB, one of the nitro oxygens approaches the methyl substituent (see Figure 5).

For 2,6-dinitroaniline (VI), the optimal interaction is similar to IA, with H-bond distances of 2.27 and 2.32 Å. There is no bifurcated structure similar to IB since there are no ortho hydrogens. The crystal structure resembles VIA, but the hydrogen

(1) The following are representative of calculations using large basis sets and correction for electron correlation: (a) Matsuoka, O.; Clementi, E.; Yoshimine, M. *J. Chem. Phys.* **1976**, *64*, 1351. (b) Clementi, E.; Habitz, P. *J. Phys. Chem.* **1983**, *87*, 2815. (c) Frisch, M. J.; Pople, J. A.; Del Bene, J. E. *J. Phys. Chem.* **1985**, *89*, 3664. (d) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 2279. (e) Del Bene, J. *J. Chem. Phys.* **1987**, *86*, 2110. (f) Diercksen, G. H. F.; Kraemer, W. P.; Roos, B. O. *Theor. Chim. Acta* **1975**, *36*, 249.

(2) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(3) Panunto, T. W.; Urbanczyk-Lipkowska, Z.; Johnson, R.; Etter, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 7786.

(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(5) (a) Dannenberg, J. J.; Vinson, L. K. *J. Phys. Chem.* **1988**, *92*, 5635. (b) Dannenberg, J. J. *J. Phys. Chem.* **1988**, *92*, 6869. (c) Galera, S.; Lluch, J. M.; Oliva, A.; Bertran, J. *THEOCHEM* **1988**, *40*, 101.

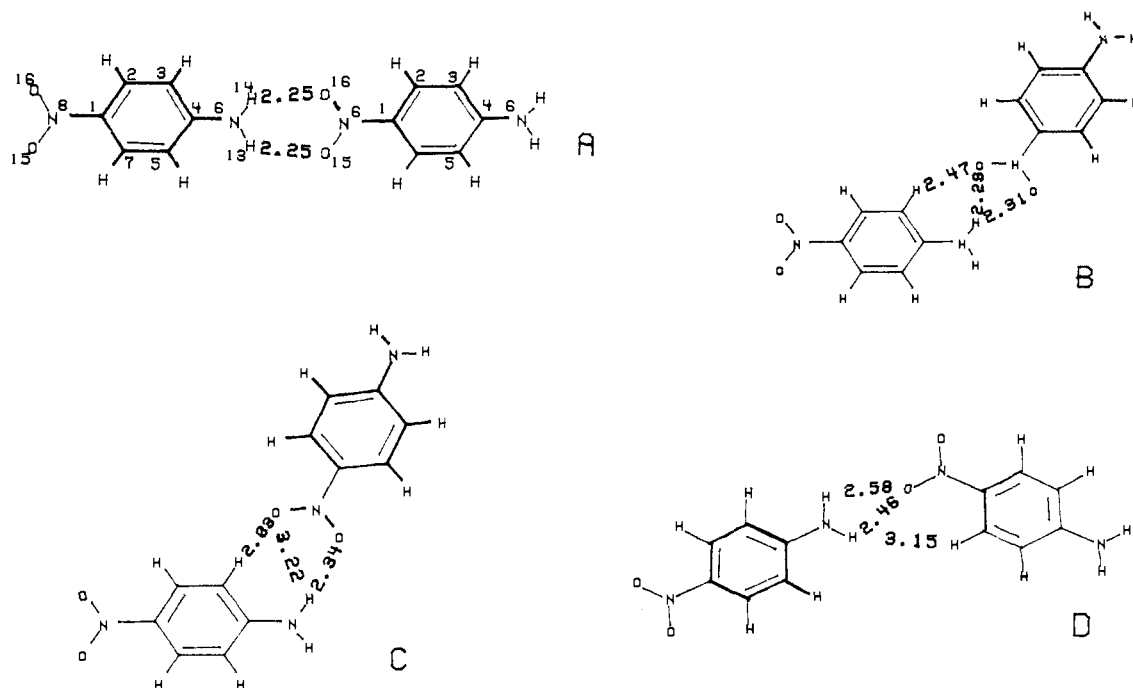


Figure 1. Structures for *p*-nitroaniline dimers IA–D. IA is the optimal dimer; IB is a relaxed dimer, with at least one H-bond, that is the local minimum closest to the crystal structure; IC is the structure obtained by fixing the H-bonds at their experimental distances and optimizing the rest. This is not a minimum (due to the constraint). See text for ID.

Table I. Heats of Formation and Interaction Energies (kcal/mol)^a

	monomer	dimer			interaction energy ^b		
		A	B	C	A	B	C
I	21.6	36.3	37.5	39.4	-6.9	-5.7	-3.7
II	20.8	36.6	36.4	36.8	-5.0	-5.2	-4.7
III	24.1	43.1	44.1	45.6	-5.0	-4.0	-2.5
IV	25.2		44.9	45.8		-5.5	-4.7
V	14.3	21.9	23.1	24.3	-6.7	-5.5	-4.2
VI	25.6	46.6		48.4	-4.5		-2.8

^aSee figures for labeling. ^bDefined as the appropriate dimer energy minus twice the corresponding monomer energy.

bond distances are substantially longer, 2.51 and 2.65 Å (see Figure 6).

Discussion

The heats of formation and hydrogen bonding energies for each of the interactions are presented in Table I. The optimal dimer interactions have bonding energies ranging from -4.5 to -8.9 kcal/mol. These values are of similar magnitude to hydrogen-bond energies for the water dimer.

The relaxed bifurcated structures I–III and VB are from 0.2 to 1.2 kcal/mol less stable than the optimal structures I–III and VA, except for II where it is 0.2 kcal/mol *more* stable. The crystal structures are generally another 0.4 to 1.9 kcal/mol less stable than the bifurcated structures.

The small destabilizations of the relaxed crystal, B, and crystal structure, C, relative to the optimal dimer are likely overcome by other interactions in the crystal such as attractions between planes and weak H-bonding between adjacent chains. For example, the amino hydrogen not involved in an H-bond in IC can form a weak interaction with a nitro group on the adjacent chain.

The interactions between the ortho hydrogens and the nitro groups that are manifest in several structures play an important role in defining the relative orientations of the nitroanilines in the crystal chains. In fact, there are two possible bifurcated structures for the dimer of I. Either (a) one amino hydrogen can interact with two nitro oxygens, as in IB, or (b) one oxygen can interact with two hydrogens, as in ID. IB, which is favored, has an additional hydrogen bond to an ortho hydrogen, while for ID, the hydrogen ortho to the nitro group is only 3.15 Å from one of the hydrogens on the amino group. What is attractive in IB becomes

repulsive in ID, whose energy is 1.6 kcal/mol higher than that of IB.

The crystal structure can be rationalized by considering the influence of interactions with the neighboring chains. For I, II, and V, the bifurcated structure leaves the second amino hydrogen more available for interactions with a neighboring chain than the more energetically favored head-on dimer. The shortening of the hydrogen bond to the ortho substituent (in C- versus B-type structures) that is often apparent may also serve to better accommodate interaction with adjacent chains or more efficient packing. For III, since the crystal interacts with both amino hydrogens instead of with the ortho hydrogen, which is more energetically favored, the ortho hydrogen rather than the amino hydrogen is left free to interact with a neighboring chain. IV resembles III in that the crystal favors an interaction with an amino-methyl hydrogen to free up the ortho hydrogen for a neighboring chain. For species VI, where the amino and nitro groups are ortho to one another, the longer hydrogen bonds in the crystal will lower the repulsions between two nitroanilines that are bound to the same monomer unit.

The geometry of the nitroaniline in the dimer is substantially different from the monomer. Pertinent geometrical parameters for the monomer and for the optimal dimer are compared in Table II. The H–N–H bond angle is 3° more on average in the dimer than in the monomer, while the O–N–O bond angle is 1° less on average. This may serve to enhance the oxygen lone-pair directionality in hydrogen bonding as found by Murray-Rust and Glusker⁶ and Vedani and Dunitz.⁷ For species III and VI where the amino and nitro groups are ortho to one another, the intramolecular hydrogen bonding seems to hinder the opening of the H–N–H angle in the dimer.

Additionally, the amino groups, which are pyramidal in the monomers, become substantially more planar in the dimers. For I, the amino hydrogens in the monomer are 13.9 and 16.8° out of the plane, while in IA, the hydrogen-bonding H's are only 0.2 and 0.6° out of the plane. Even the amino hydrogens not involved in hydrogen bonding are 0.3 and 0.5° out of the plane. This same trend is observed for the other species though not to the same extent.

(6) Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018.
(7) Vedani, A.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 7653.

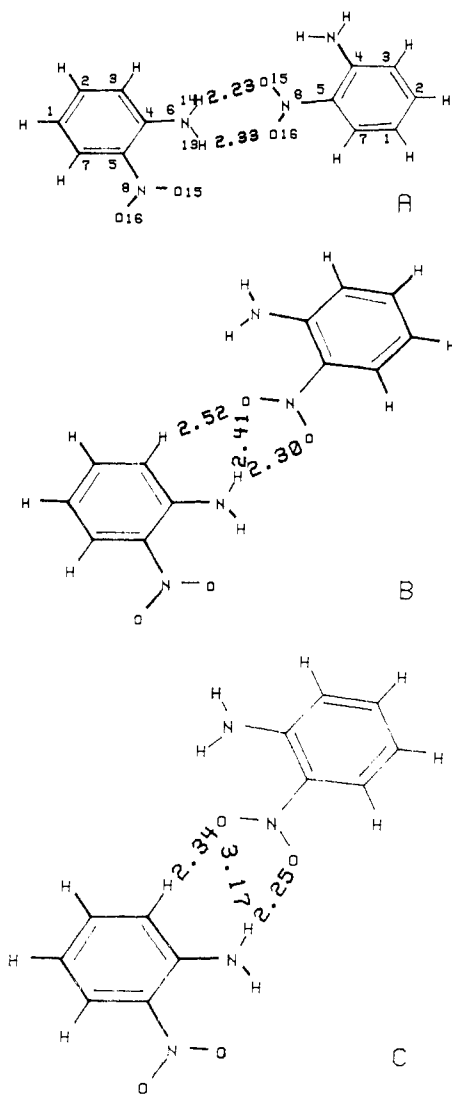


Figure 2. Structures for *o*-nitroaniline dimers IIA-C (structures are labeled as in Figure 1).

Table II. Relevant Angles (degrees) in the Monomers and Dimers^a

	NH ₂ dihedral						
	monomer	dimer		H-N-H angle		O-N-O angle	
		A	B	monomer	dimer	monomer	dimer
I	13.9	0.2	0.3	116.9	118.5	121.7	120.6
	16.8	0.6	0.5				
II	7.5	0.2	5.7	118.3	117.8	120.7	120.2
	7.9	1.9	9.8				
III	19.3	5.3	16.6	114.4	118.6	122.0	121.2
	23.8	6.8	22.6				
IV	6.7	9.0	4.7	117.7	118.3	121.7	120.4
	10.6	9.9	5.4				
V	14.4	0.3	5.0	116.7	119.2	121.7	120.9
	18.1	1.9	5.8				
VI	0.3	0.4	1.5	117.2	116.1	121.1	120.4
	5.4	2.0	5.4				

^a Dimer A is that providing the NH₂ that H-bonds (on the left in the figures). The Dihedral angles refer to the plane of the aromatic ring. The valence angles refer to the NH₂ and NO₂ groups involved in the H-bonds. The figures are for the most stable dimer of each monomer.

The differences in the calculated geometrical parameters of the isolated molecules and the H-bonding dimers (which are models for the gas and solid phases) serve to emphasize the potential errors that may arise upon comparison of calculated geometrical parameters for isolated molecules with crystal structural data. It is significant that the calculated optimized geometries, themselves, change when intermolecular interactions that simulate the solid

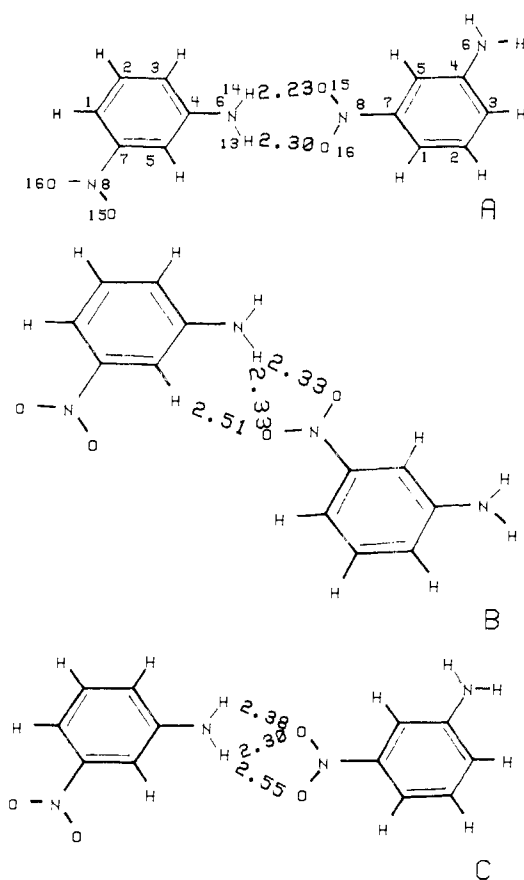


Figure 3. Structures for *m*-nitroaniline dimers IIIA-C (structures are labeled as in Figure 1).

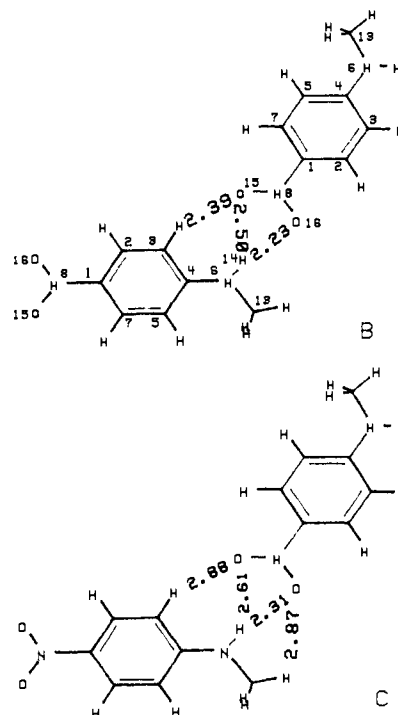


Figure 4. Structures for *N*-methyl *p*-nitroaniline dimers IVB-C (structures are labeled as in Figure 1).

phase are explicitly considered. This observation strongly suggests that application of molecular orbital methods to dimers or small aggregates may be useful for modelling the geometries of molecules in the solid phase. Molecular orbital modelling of individual molecules is properly compared with experimental observations

Table III. Charge Distributions for Dimers I-VI

atom	monomer	dimer A	dimer B	dimer C	atom	monomer	dimer A	dimer B	dimer C
A. Dimers IA-C									
C-1 A	-0.197	-0.222	-0.218	-0.215	C-7 A	-0.018	-0.009	-0.012	-0.014
C-1 B	-0.197	-0.209	-0.209	-0.210	C-7 B	-0.018	-0.005	-0.006	-0.005
C-2 A	-0.016	-0.009	-0.015	-0.013	N-8 A	0.577	0.581	0.579	-0.580
C-2 B	-0.016	-0.005	-0.006	-0.007	N-8 B	0.577	0.582	0.580	0.585
C-3 A	-0.225	-0.246	-0.234	-0.236	H-13 A	0.217	0.244	0.225	0.224
C-3 B	-0.225	-0.236	-0.236	-0.237	H-13 B	0.217	0.236	0.235	0.235
C-4 A	0.139	0.175	0.172	0.173	H-14 A	0.217	0.246	0.253	0.248
C-4 B	0.139	0.173	0.172	0.176	H-14 B	0.217	0.235	0.234	0.233
C-5 A	-0.224	-0.246	-0.247	-0.248	O-15 A	-0.370	-0.381	-0.381	-0.382
C-5 B	-0.224	-0.237	-0.235	-0.236	O-15 B	-0.370	-0.388	-0.389	-0.395
N-6 A	-0.357	-0.371	-0.376	-0.381	O-16 A	-0.370	-0.381	-0.381	-0.380
N-6 B	-0.357	-0.377	-0.381	-0.381	O-16 B	-0.370	-0.391	-0.387	-0.378
B. Dimers IIA-C									
C-1 A	-0.204	-0.217	-0.215	-0.211	C-7 A	-0.022	-0.019	-0.021	-0.025
C-1 B	-0.204	-0.201	-0.203	-0.203	C-7 B	-0.022	-0.018	-0.018	-0.018
C-2 A	-0.036	-0.037	-0.041	-0.042	N-8 A	0.582	0.582	0.583	0.582
C-2 B	-0.036	-0.031	-0.029	-0.029	N-8 B	0.582	0.582	0.582	0.588
C-3 A	-0.236	-0.241	-0.236	-0.233	H-13 A	0.260	0.270	0.260	0.257
C-3 B	-0.236	-0.236	-0.237	-0.237	H-13 B	0.260	0.258	0.261	0.263
C-4 A	0.195	0.207	0.208	0.195	H-14 A	0.227	0.244	0.252	0.246
C-4 B	0.195	0.198	0.204	0.205	H-14 B	0.227	0.231	0.234	0.233
C-5 A	-0.235	-0.250	-0.253	-0.245	O-15 A	-0.399	-0.393	-0.402	-0.402
C-5 B	-0.235	-0.235	-0.240	-0.241	O-15 B	-0.399	-0.420	-0.415	-0.407
N-6 A	-0.367	-0.357	-0.360	-0.358	O-16 A	-0.361	-0.377	-0.375	-0.372
N-6 B	-0.367	-0.365	-0.367	-0.368	O-16 B	-0.361	-0.364	-0.376	-0.388
C. Dimers IIIA-C									
C-1 A	-0.117	-0.143	-0.142	-0.144	C-7 A	-0.086	-0.073	-0.076	-0.072
C-1 B	-0.117	-0.118	-0.116	-0.126	C-7 B	-0.086	-0.078	-0.080	-0.071
C-2 A	-0.099	-0.090	-0.092	-0.090	N-8 A	0.564	0.563	0.564	0.563
C-2 B	-0.099	-0.094	-0.094	-0.089	N-8 B	0.564	0.565	0.565	0.563
C-3 A	-0.159	-0.187	-0.187	-0.190	H-13 A	0.200	0.239	0.244	0.242
C-3 B	-0.159	-0.160	-0.159	-0.171	H-13 B	0.200	0.207	0.205	0.221
C-4 A	0.066	0.125	0.117	0.122	H-14 A	0.197	0.239	0.219	0.233
C-4 B	0.066	0.080	0.074	0.111	H-14 B	0.197	0.206	0.204	0.221
C-5 A	-0.144	-0.173	-0.160	-0.173	O-15 A	-0.360	-0.365	-0.363	-0.364
C-5 B	-0.144	-0.153	-0.150	-0.165	O-15 B	-0.360	-0.377	-0.376	-0.354
N-6 A	-0.336	-0.393	-0.388	-0.384	O-16 A	-0.357	-0.364	-0.366	-0.364
N-6 B	-0.336	-0.343	-0.341	-0.379	O-16 B	-0.357	-0.366	-0.363	-0.389
D. Dimers IVB,C									
C-1 A	-0.202		-0.216	-0.214	C-7 A	-0.015		-0.016	-0.015
C-1 B	-0.202		-0.206	-0.211	C-7 B	-0.015		-0.009	-0.010
C-2 A	-0.018		-0.018	-0.016	N-8 A	0.579		0.580	0.580
C-2 B	-0.018		-0.010	-0.010	N-8 B	0.579		0.579	0.582
C-3 A	-0.228		-0.230	-0.232	H-10 A	0.144		0.164	0.156
C-3 B	-0.228		-0.232	-0.232	C-13 A	-0.076		-0.068	-0.006
C-4 A	0.153		0.168	0.165	C-13 B	-0.076		-0.073	-0.072
C-4 B	0.153		0.168	0.167	H-14 A	0.230		0.257	0.252
C-5 A	-0.224		-0.241	-0.239	O-15 A	-0.372		-0.382	-0.380
C-5 B	-0.224		-0.230	-0.230	O-15 B	-0.372		-0.384	-0.375
N-6 A	-0.327		-0.328	-0.326	O-16 A	-0.372		-0.381	-0.380
N-6 B	-0.327		-0.330	-0.331	O-16 B	-0.372		-0.392	-0.394
E. Dimers VA-C									
C-1 A	-0.192	-0.217	-0.213	-0.212	C-7 A	-0.022	-0.012	-0.015	-0.014
C-1 B	-0.192	-0.204	-0.202	-0.211	C-7 B	-0.022	-0.010	-0.010	-0.006
C-2 A	-0.021	-0.011	-0.017	-0.018	N-8 A	0.577	0.580	0.580	0.580
C-2 B	-0.021	-0.009	-0.011	-0.012	N-8 B	0.577	0.583	0.578	0.584
C-3 A	-0.158	-0.182	-0.170	-0.169	C-10 A	-0.175	-0.170	-0.172	-0.174
C-3 B	-0.158	-0.171	-0.168	-0.171	C-10 B	-0.175	-0.175	-0.175	-0.175
C-4 A	0.136	0.175	0.170	0.171	H-13 A	0.215	0.245	0.228	0.228
C-4 B	0.136	0.172	0.167	0.175	H-14 A	0.217	0.247	0.254	0.251
C-5 A	-0.222	-0.245	-0.244	-0.244	O-15 A	-0.370	-0.381	-0.380	-0.379
C-5 B	-0.222	-0.234	-0.232	-0.236	O-15 B	-0.370	-0.392	-0.379	-0.392
N-6 A	-0.352	-0.369	-0.372	-0.372	O-16 A	-0.370	-0.381	-0.381	-0.379
N-6 B	-0.352	-0.373	-0.371	-0.379	O-16 B	-0.370	-0.387	-0.396	-0.378
F. Dimers VIA,C									
C-1 A	-0.222	-0.231		-0.227	C-4 B	0.259	0.265		0.260
C-1 B	-0.222	-0.223		-0.221	C-5 A	-0.255	-0.263		-0.261
C-2 A	0.027	0.027		0.026	C-5 B	-0.255	-0.258		-0.257
C-2 B	0.027	0.032		0.030	C-7 A	0.028	0.027		0.026
C-3 A	-0.256	-0.262		-0.260	C-7 B	0.028	0.029		0.026
C-3 B	-0.256	-0.254		-0.255	H-13 A	0.268	0.274		0.274
C-4 A	0.259	0.265		0.260	H-14 A	0.271	0.281		0.281

Table III (Continued)

atom	monomer	dimer A	dimer B	dimer C	atom	monomer	dimer A	dimer B	dimer C
N-6 A	-0.338	-0.320		-0.322	O-15 B	-0.384	-0.387		-0.386
N-6 B	-0.338	-0.329		-0.331	O-16 A	-0.347	-0.355		-0.354
N-8 A	0.582	0.583		0.582	O-16 B	-0.347	-0.347		-0.347
N-8 B	0.582	0.584		0.584	O-33 A	-0.351	-0.358		-0.356
N-11 A	0.585	0.582		0.583	O-33 B	-0.351	-0.362		-0.362
N-11 B	0.583	0.580		0.581	O-34 A	-0.386	-0.383		-0.381
O-15 A	-0.384	-0.387		-0.385	O-34 B	-0.386	-0.393		-0.389

^aCharges are in units of electronic charge. See figures for numbering conventions. "A" refers to the monomer supplying the NH₂ to the H-bonding interaction (on the left in the figures), "B" to the other.

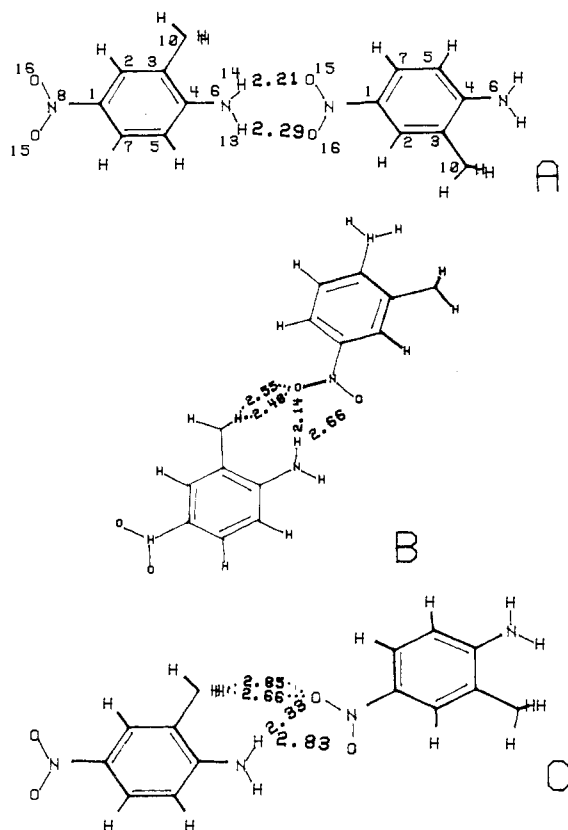


Figure 5. Structures for *p*-nitro-*o*-toluidine dimers VA,C (structures are labeled as in Figure 1).

of the molecular properties of gas-phase molecules. Further work in this direction will be necessary before more definite conclusions can be reached.

Inspection of the net atomic charges in the monomers and dimers (Table III) indicates that there is increased charge alternation in the dimer. This suggests that mutual polarization might be occurring. The net charge transfer is very small (<0.01 electron in all cases). In an infinite crystal, all units must be neutral. The small degree of charge transfer observed in the dimer supports the appropriateness of the dimer as a model for the crystal. In the cases where H-bonds to ortho hydrogens are implicated, the charge increases substantially on the ortho hydrogen upon dimer formation.

The charge polarization, and the planarization of the nitroanilines upon dimer formation, suggests that increasing the H-bonded chain beyond two molecules should result in greater stabilization (per monomer-monomer interaction) since whatever

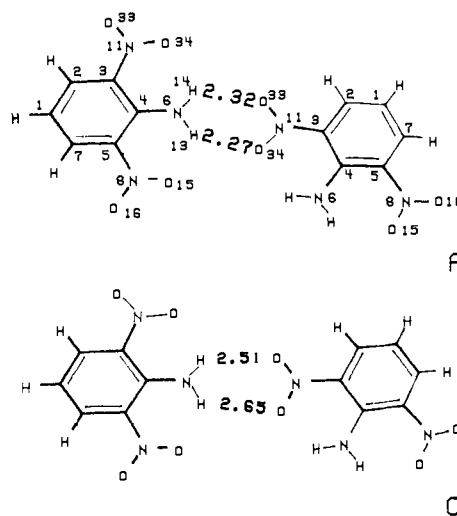


Figure 6. Structures for 2,6-dinitroaniline dimers VIA,C (structures are labeled as in Figure 1).

energy that is required to distort the monomer to its planar, polarized state is already overcome for both molecules at the dimer stage. Adding an additional monomer would require only one (rather than two) additional distortion.

With the exception of III and VI, all of the crystal structures strongly resemble the relaxed crystal dimer structure (B). In the case of III, structure IIIB would require a bend in the crystal chain that might be very difficult to accommodate, while in the case of VI, the B structure cannot exist because of the absence of hydrogens ortho to the amino group.

Conclusion

AM1 calculations on the dimers of nitroanilines are of considerable value in analyzing their crystal structures. In particular, the intermolecular forces that dictate the relative orientations of the individual molecules in the crystal chains can be understood. It is likely that this methodology will be useful for modelling the kinds of interactions that might occur in other crystals.

The present calculations suggest that the differences in molecular geometry between gas and solid (crystal) phases may be largely manifest in aggregates as small as dimers. If this is the case, molecular orbital theory may be extremely useful as a tool for understanding these differences.

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

Registry No. I, 100-01-6; II, 88-74-4; III, 99-09-2; IV, 100-15-2; V, 99-52-5; VI, 606-22-4.