

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231461877>

# Conformational polymorphism.2. Crystal energetics by computational substitution—Further evidence for sensitivity of method

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · SEPTEMBER 1978

Impact Factor: 12.11 · DOI: 10.1021/ja00488a012

---

CITATIONS

34

---

READS

23

## 2 AUTHORS:



**Arnie Hagler**

University of Massachusetts Amherst

134 PUBLICATIONS 7,988 CITATIONS

SEE PROFILE



**Joel Bernstein**

New York University Abu Dhabi (NYUAD), Ben...

170 PUBLICATIONS 8,580 CITATIONS

SEE PROFILE

a complex band form due to vibrational excitations. In the absence of sufficient experimental information one can only state that only four IPs are to be assigned to the second band system and these are the  $6b_u(n-)$  (14.70 eV),  $2b_g(\pi)$  (15.22 eV),  $2a_u(\pi)$  (15.69 eV), and  $6a_g$  (15.98 eV) IPs. The CNDO-type calculations<sup>2a</sup> lead, incidentally, to the same conclusion that only four IPs should be assigned to the second band system, but they do not lead to the same ordering of states. The  $5b_u$  IP is to be assigned to the third band at 17.05 eV and the  $5a_g$  IP to the sharp and intense fourth band at 18.01 eV. The last band discernible in the spectrum at 18.69 eV is associated with the  $1b_g(\pi)$  and the  $4b_u$  IPs. The last  $\pi$  IP ( $1a_u(\pi)$ ) is to be expected at 19.83 eV; i.e., both the  $1b_g(\pi)$  and the  $1a_u(\pi)$  IPs are found at considerably higher energies than initially expected. Since the lowest unoccupied orbital is of  $a_u$  symmetry and the highest occupied orbital of  $a_g$  symmetry one may expect low-lying poles of the self-energy part of  $a_u$  symmetry. If this is the case the calculated value of the  $1a_u$  IP is unreliable and a different approach should be used.<sup>2b</sup>

The theoretical calculations thus lead to a substantial revision of the assignment of the PES of *trans*-oxalyl fluoride. Assuming the extension of the basis set to be of minor impor-

tance for this molecule the ordering of ionic states can be unambiguously established. It also becomes apparent that more work on this molecule is required in order to elucidate the equilibrium among the various rotational isomers which can contribute to the bands in the PES and to determine their structures.

## References and Notes

- (1) (a) Technische Universität Braunschweig; (b) Max-Planck-Institut für Physik und Astrophysik; (c) Universität Freiburg.
- (2) (a) D. C. Frost, C. A. McDowell, G. Pouzard, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, **10**, 273 (1977); (b) L. S. Cederbaum, *Theor. Chim. Acta*, **31**, 239 (1973); *J. Phys. B*, **8**, 290 (1975); L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.*, **36**, 205 (1977).
- (3) W. von Niessen, L. S. Cederbaum, and G. H. F. Dierksen, *J. Chem. Phys.*, **67**, 4124 (1977).
- (4) Preliminary results, private communication by K. Hedberg.
- (5) G. H. F. Dierksen and W. P. Kraemer, MUNICH, Molecular Program System, Reference Manual, Special Technical Report, Max-Planck-Institut für Physik und Astrophysik, to be published; G. H. F. Dierksen, *Theor. Chim. Acta*, **33**, 1 (1974).
- (6) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
- (7) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1933).
- (8) L. S. Cederbaum, *Chem. Phys. Lett.*, **25**, 562 (1974).
- (9) D. P. Chong, F. G. Herring, and D. McWilliams, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 445 (1975).
- (10) W. von Niessen, *J. Am. Chem. Soc.*, **99**, 7151 (1977).

## Conformational Polymorphism. 2. Crystal Energetics by Computational Substitution. Further Evidence for the Sensitivity of the Method

A. T. Hagler\*<sup>1a</sup> and J. Bernstein\*<sup>1b</sup>

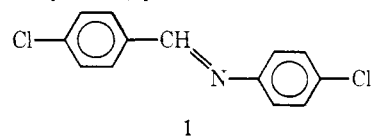
Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801, and the Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel. Received November 14, 1977

**Abstract:** The effect of crystal forces on molecular conformations has been investigated using a combination of experimental X-ray crystallography and theoretical lattice energy and ab initio calculations. We have extended techniques developed previously which take advantage of and rationalize the phenomena of conformational polymorphism—the existence of two or more crystal forms of the same molecule existing in significantly different conformations. Lattice energy calculations in conjunction with ab initio molecular orbital studies on the model compound *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline have been applied to answer the question as to why this molecule does not pack in a structure containing the ordered, low-energy, molecular conformation. The molecule was packed in the  $P2_1$  lattice containing its dimethyl analogue. The lattice energy was minimized with three different potentials and the results were analyzed in terms of “partial atomic energy” contributions. All potentials showed the structure of the dichloro compound to be less stable than either the stable *Pccn* or metastable *PI* observed structures (by 1.5 and 2.5 kcal, respectively). The analysis in terms of the partial atomic energies showed the relative lack of stability to arise from the relatively unfavorable energetic environments of the aniline ring (including its Cl) as compared with its environment in the observed crystals. Finally comparison of the total energies (lattice plus intramolecular energy as obtained by molecular orbital calculations) accounted for the “observed nonexistence” of the low-energy conformation structure.

In the first paper in this series<sup>2a</sup> we presented a newly developed technique for investigating the influence of crystal forces on molecular conformation. The phenomenon of conformational polymorphism is a particularly suitable basis for such studies since we take advantage of the fact that a flexible molecule may crystallize in polymorphic crystal forms in which the molecules adopt significantly different molecular conformations. If these conformations differ in energy, then the crystal forces must supply the energy to stabilize the more highly energetic molecular conformation. When the crystal structures differ between the polymorphs then the differences in the packing between the forms lead to these energy differences. For the crystal forms and molecules involved, the thorough investigation of these forces requires (1) full detailed crystal structure analyses to determine molecular geometries

and intermolecular relationships, (2) calculations of molecular energetics to obtain reliable estimates of the energetics of different molecular conformations, (3) lattice energy minimizations to obtain differences in crystal energies between the crystal forms, and (4) detailed analysis of the differences in packing and individual atomic contributions to the crystal energy to determine the particular crystal forces which stabilize one molecular conformation over another.

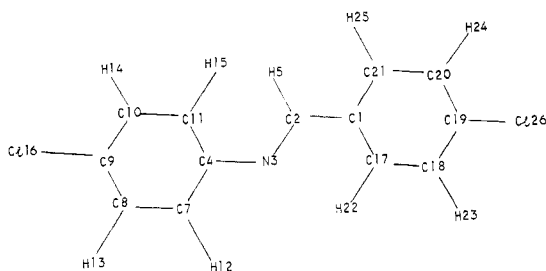
Such an analysis was previously carried out on the system *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (**1**). The material



**Table I.** Nonbonded Parameters and Partial Charges Employed in Lattice Energy Minimizations

atom type	6-12 <sup>a</sup>		6-9 <sup>a</sup>		exponential <sup>b</sup>			partial charges <sup>d</sup>
	<i>r</i> <sup>*</sup>	$\epsilon$	<i>r</i> <sup>*</sup>	$\epsilon$	<i>A</i>	<i>B</i>	$\alpha$	
C	4.35	0.039	3.62	0.184	449.7	71 500	3.60	0.11, -0.06, 0.026
N	3.93	0.167	4.01	0.161	449.7	71 500	3.60	-0.27
H	2.75	0.038	3.54	0.0025	40.2	2870	3.74	0.072
Cl <sup>c</sup>	3.866	0.244	3.866	0.244	1430	220 700	3.621	-0.14

<sup>a</sup> See ref 8. <sup>b</sup> Potential has form  $-Ar^6 + B \exp(-\alpha r)$ . Except for chlorine, these parameters taken from ref 9. <sup>c</sup> Reference 11. <sup>d</sup> Charges based on ab initio calculations on model compounds (see ref 2a). They were assigned as follows: C1, C2, C4, 0.11; C9, C19, 0.026; the remainder, -0.06.



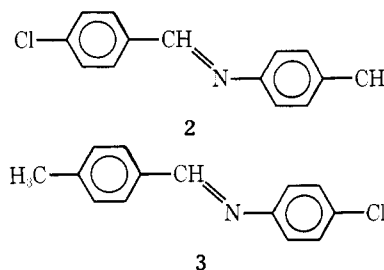
**Figure 1.** Numbering scheme for **1**. Numbering is consistent with previous study<sup>2a</sup> which had an additional hydrogen (H6) on the bridge (due to disorder), which is not present in the ordered structure studied here.

is dimorphic and exhibits crystallographic disorder in both forms. In the triclinic form,<sup>2b</sup> the disorder is about a center of symmetry and the molecule adopts a planar conformation. In the orthorhombic form,<sup>3</sup> the disorder is about a twofold crystallographic axis and the phenyl rings are rotated by equal but opposite amounts (24.8°) about the N-phenyl and CH-phenyl bonds. These two torsional parameters are sufficient to define the molecular conformation.

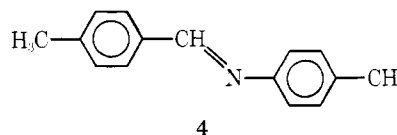
Our previous results can be summarized briefly as follows. Lattice energy minimizations yielded a lower (more negative) energy for the triclinic structure by an amount compatible with the molecular conformational energy difference obtained from the ab initio molecular orbital calculations. This must be so if we are to account for the stabilization of the more highly energetic planar conformation in the triclinic form<sup>4,5</sup> over the nonplanar one in the orthorhombic form. In addition, the detailed analysis of the energetics based on a partitioning of the total energy into partial atomic contributions for each of the forms led to a number of conclusions. The relative (ranked) energy contribution of the individual atoms is the same for both crystal forms. Second, the largest single contributor to the total lattice energy in both forms is the chlorine substituent; however, it has essentially the same energetic environment in the two forms, and makes no significant contribution to the difference in lattice energies between the two forms. Third, no one atom or group of atoms dominates in stabilizing the triclinic form over the orthorhombic form, but nearly all atoms do make some contribution in an overall cooperative effect.

The results were quantitatively consistent for the system studied and with the energetic and conformational data available for benzylideneaniline.<sup>5</sup> It was not clear, however, whether the conclusions based on the analyses of the partitioned atomic energies were characteristic of conformational polymorphs or were indigenous to the particular system studied. Also, the disorder observed in both crystal forms is not characteristic of many molecular crystals, and although it did not complicate our previous analysis, we wished to extend this type of study to nondisordered molecular crystals. Finally, and perhaps of most interest, the question arises as to why the molecule does not pack in a crystal in which the intramolecular energy is a minimum. In general this would be an extremely difficult problem to attack, as there is no information available as to the "nonexistent" favorable packing mode of the low-energy molecular form. In this molecular system, however, if

the chlorines are substituted by methyls, one of the three resulting polymorphic forms contains the low-energy molecular conformation. Since the size of a chlorine atom does not differ greatly from that of a methyl group, this would appear to be a reasonable packing for the dichloro derivative as well. The similarity of the chlorine and methyl substituents is demonstrated by the fact that the "hybrid" molecules **2** and **3** are crystallographically isomorphous and the space group symmetry ( $P2_1/a$ ) and the contents of the cell ( $Z = 2$ ) require disorder and with it crystallographic and energetic equivalence of these two substituents.<sup>7</sup> Thus this final question is amenable to attack as described below.



The dimethyl analogue **4** of the compound studied previously is trimorphic,<sup>6</sup> and affords a suitable system for investigating the points raised above. As noted above, form II of **4** is not di-

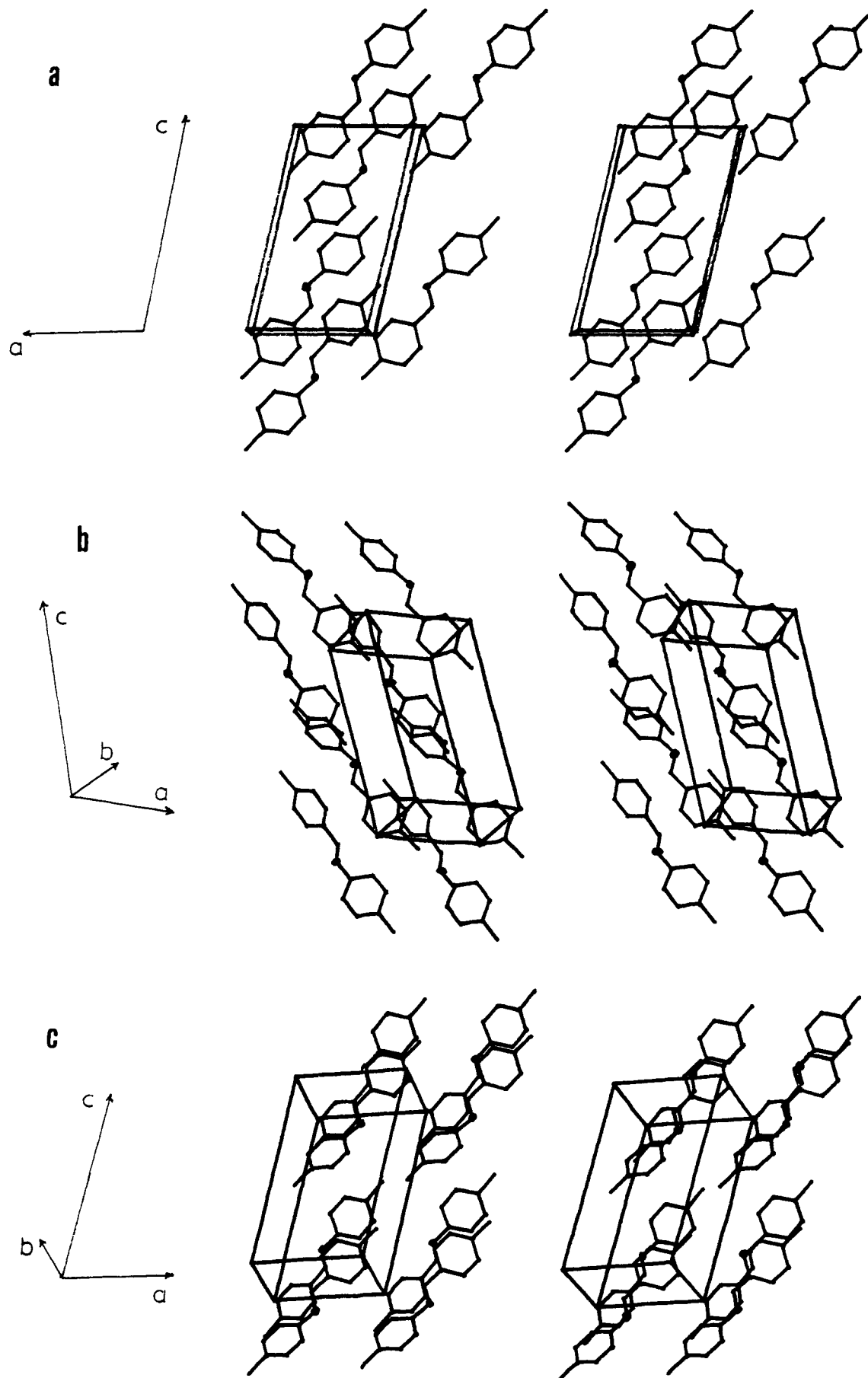


sordered<sup>6b</sup> and the molecular conformation found therein approximates that for the lowest free molecule energy:<sup>4,5</sup> a torsion angle of 41.7° about the N-phenyl bond and -3.0° about the CH-phenyl bond. The second known crystal structure of **4**<sup>6a</sup> has positional as well as crystallographic disorder and thus is not well suited to the type of analysis carried out here. The crystal structure of the third form is currently under study. If the analysis of conformational polymorphs based on partial atomic energies is valid, then placing the dichloro compound in the crystal structure of **4** should afford an answer to the question of why **1** does not pack in this ordered, low intramolecular energy structure.

### Calculations

Lattice energy calculations were carried out using techniques described previously.<sup>2a,8</sup> Once again to avoid "potential-dependent" results we employed three different potential functions in all of the calculations: 6-12, 6-9, and Williams<sup>9</sup> exponential functions. Parameters employed for the atoms as numbered in Figure 1 are unchanged from the previous paper,<sup>2a</sup> except for the C, H, and N atoms on the bridge, which were assigned "average" values in the previous work<sup>2a</sup> to account for the disorder in the triclinic and orthorhombic forms.

Form II of **4** crystallizes in the chiral monoclinic space group  $P2_1$ . A stereoview of the structure down the *b* axis is given in Figure 2a. Using the coordinates obtained from the crystal



**Figure 2.** Various views of the crystal structure of form II of **2**. The heavy dot denotes the nitrogen atom in all views. In all cases the view includes the reference molecule in the published structure<sup>6b</sup> and three additional molecules related by translations along the *a* and *c* axes. The remaining molecules are related by the twofold screw axes parallel to *b*. (a) View down the *b* axis. (b) View on the benzylidene plane of the reference molecule. (c) View on the aniline plane of the reference molecule.

Table II

A. Summary of Lattice Energy Calculations									
crystal energy, kcal/mol				crystal energy, kcal/mol					
<div>6-12      exponential      6-9</div>				<div>6-12      exponential      6-9</div>					
monoclinic form				orthorhombic form <sup>a</sup>					
initial	$E_{\text{tot}}$	-19.19	-20.34	-36.65	initial	$E_{\text{tot}}$	-19.34	-21.53	-39.81
	$E_{\text{nb}}$	-20.05	-21.20	-37.51		$E_{\text{nb}}$	-20.66	-22.85	-41.13
	$E_{\text{elec}}$	0.86	0.86	0.86		$E_{\text{elec}}$	1.32	1.32	1.32
final	$E_{\text{tot}}$	-20.13	-20.75	-41.23	final	$E_{\text{tot}}$	-21.68	-22.34	-42.73
	$E_{\text{nb}}$	-20.74	-21.48	-42.05		$E_{\text{nb}}$	-22.41	-23.27	-44.24
	$E_{\text{elec}}$	0.61	0.73	0.82		$E_{\text{elec}}$	0.73	0.93	1.51
					$\Delta E_{\text{tot}}^b$		1.55	1.59	1.50
Lattice Parameters and Shifts upon Minimization									
experimental		6-12		exponential		6-9			
$a$ ( $\Delta a$ ), Å	6.891	7.002 (0.111)		7.021 (0.130)		6.845 (-0.046)			
$b$ ( $\Delta b$ )	7.153	7.621 (0.468)		7.120 (-0.033)		6.606 (-0.547)			
$c$ ( $\Delta c$ )	12.600	12.394 (-0.206)		12.490 (-0.110)		12.176 (-0.424)			
$\alpha$ ( $\Delta\alpha$ ), deg	90.0	90.0 (0.0)		90.0 (0.0)		90.0 (0.0)			
$\beta$ ( $\Delta\beta$ )	102.7	105.3 (2.6)		105.5 (2.8)		107.7 (5.1)			
$\gamma$ ( $\Delta\gamma$ )	90.0	90.0 (0.0)		90.0 (0.0)		90.0 (0.0)			
$V$ ( $\Delta V$ ), Å <sup>3</sup>	605.9	637.9 (31.9)		601.6 (-4.3)		524.4 (-81.5)			
B. Comparison of Intramolecular and Intermolecular Energies <sup>c,d</sup>									
structure	exocyclic angles		intramolecular contribution, kcal/mol			intermolecular energies, kcal/mol			
	$\alpha$	$\beta$	$\alpha$	$\beta$	total	6-12	exponential	6-9	
$P2_1$	41.7	-3.0	-2.1	0	-2.1	-20.13	-20.75	-41.23	
$Pccn$	24.8	-24.8	-1.7	1.0	-0.7	-21.68	-22.34	-42.73	
$P\bar{1}$	0.4	0.4	0	0	0	-22.73	-23.99	-45.71	

<sup>a</sup> Reference 2a. <sup>b</sup>  $\Delta E_{\text{tot}}$  = this result minus that for orthorhombic crystal. <sup>c</sup>  $\alpha$  is the angle about the N-phenyl bond and  $\beta$  is the angle about the CH-phenyl bond. The signs are defined in ref 3. <sup>d</sup> 0° is defined as the reference (zero level) of energy. Details of these calculations are given in ref 4c.

structure analysis<sup>6b</sup> we generated coordinates for chlorine atoms to replace the methyl groups with idealized trigonal geometry at the substituted carbon and C-Cl bond length of 1.735 Å.<sup>10</sup> Hydrogen atom positions were similarly included with a C-H bond length of 1.08 Å. Lattice energy minimizations were carried out exclusively on the dichloro compound in the crystal structure of form II of **4**.

## Results and Discussion

The energy and structure resulting from the lattice energy minimization are summarized and compared with those obtained for the orthorhombic form of **1** in Table II. The partial atomic energies are given in Table III and compared there with the orthorhombic form (the higher lattice energy form of the two "true" polymorphs).

As in our previous study the quantitative agreement between the minimizations employing the 6-12 and exponential potentials is excellent with rather large energy differences encountered between them and the minimization employing the 6-9 potential. However, except for this discrepancy in total energy which we encountered earlier, all conclusions regarding differences between crystal forms and packing details are valid for the 6-9 calculations. The total minimized crystal energies obtained for the 6-12 and exponential potentials are probably quite close to the true sublimation energy, which is estimated to be 20-24 kcal/mol.<sup>2a</sup> Hence, once again it is the 6-9 potential which yields an overestimate for the lattice energy.

All three potentials lead to minimized lattice energies indicating that the crystal composed of molecule **1** in form II of **4** is less stable than the orthorhombic form of **1** by about 1.5

kcal/mol, and consequently less stable than the triclinic form by about 2.5 kcal/mol. This is the magnitude of the energy difference expected between polymorphs<sup>12,13</sup> and is in very good agreement with the approximate estimates of the difference in intramolecular energy as summarized in Table IIB. It not only accounts for the stability of the orthorhombic form over the ordered structure but also the excess stability of the metastable triclinic form over the  $P2_1$  structure. Both the stable  $Pccn$  and metastable  $P\bar{1}$  forms are calculated to be slightly more stable overall (intra- plus intermolecular energies) by approximately the same magnitude than the hypothetical  $P2_1$  structure.

The partitioned atomic energies are given in Table III, together with their relative ranking in increasing energy, and the difference between the atom's contribution in this structure and the orthorhombic structure of **1**. The overall consistency of the results with respect to the various potentials employed is again evident from the general agreement in the rankings. Thus, in this case, as earlier, the conclusions which may be drawn from this study are independent of the potential employed.

Analysis of the partitioned energy is most conveniently carried out by examining the contributions from certain atomic groups, as follows: I, "chlorine region", a, C9, Cl 16; b, C19, Cl 26; II, "bridge", Cl, C2, N3, C4, H5; III, aniline ring, C7, C8, C10, C11, H12, H13, H14, H15; IV, benzylidene ring, C17, C18, C20, C21, H22, H23, H24, H25. Owing to disorder in the triclinic and orthorhombic structures of I, groups Ia and Ib are crystallographically (and consequently energetically) equivalent, as are groups III and IV. Here, in the absence of disorder, the crystallographic requirement of equivalency is

**Table III.** Partition of the Minimized Crystal Energy into Individual Atomic Contributions ( $e_i$ )<sup>a</sup> for Three Potentials Employed

atom	6-12			exponential			6-9		
	$e_i$	rank <sup>b</sup>	$\Delta e_i$ <sup>c</sup>	$e_i$	rank <sup>b</sup>	$\Delta e_i$ <sup>c</sup>	$e_i$	rank <sup>b</sup>	$\Delta e_i$ <sup>c</sup>
C1	-0.17	21	-0.02	-0.23	21	-0.02	-1.66	16	-0.13
C2	-0.41	19	<i>1.50</i>	-0.50	17	<i>1.37</i>	-1.94	15	<i>1.77</i>
N3	-1.81	3	0.10	-1.46	2	0.41	-3.18	3	0.53
C4	-1.04	8	-0.89	-1.14	8	-0.93	-2.54	8	-1.01
H5	-0.11	22	-0.15	0.03	22	0	0.33	22	-0.03
C7	-0.70	13	<i>0.48</i>	-0.86	13	<i>0.53</i>	-2.29	12	<i>0.71</i>
C8	-0.62	16	0.36	-0.84	14	0.30	-2.33	11	0.25
C9	-0.98	9	0.14	-1.02	9	0.07	-2.41	10	0.16
C10	-0.62	15	<i>0.74</i>	-0.72	15	<i>0.88</i>	-1.98	14	<i>1.27</i>
C11	-0.72	12	<i>0.80</i>	-0.91	11	<i>0.83</i>	-2.25	13	<i>1.18</i>
H12	-0.87	10	-0.47	-0.87	12	-0.55	-0.72	17	-0.76
H13	-0.54	17	-0.08	-0.42	19	0.08	0.01	20	0.44
H14	-0.65	14	-0.82	-0.61	16	-0.97	-0.37	18	-1.13
H15	-0.05	23	-0.48	0.05	23	-0.53	0.53	23	-0.69
Cl 16	-1.93	2	<i>0.52</i>	-1.78	3	<i>0.50</i>	-2.96	6	<i>0.32</i>
C17	-1.27	5	0.25	-1.54	5	0.20	-3.11	4	0.32
C18	-1.51	4	-0.15	-1.71	4	-0.11	-3.45	2	-0.20
C19	-0.85	11	-0.01	-0.94	10	0.15	-2.54	9	0.03
C20	-1.25	6	-0.27	-1.35	7	-0.22	-2.88	7	-0.30
C21	-1.24	7	-0.06	-1.43	6	-0.04	-2.96	5	0.04
H22	0.12	24	-0.31	0.35	24	-0.23	0.72	24	-0.50
H23	0.24	25	0.07	0.42	25	0.06	0.73	25	-0.03
H24	-0.43	18	0.19	-0.46	18	0.04	-0.25	19	0.18
H25	-0.19	20	0.21	-0.16	21	0.16	0.03	21	-0.01
Cl 26	-2.44	1	0.01	-2.57	1	-0.19	-3.85	1	-0.57

<sup>a</sup> Entries for  $e_i$  and  $\Delta e_i$  are in kcal/mol. The totals of the entries in the columns differ slightly from those given in Table II owing to cumulative errors in rounding and subtraction. <sup>b</sup> In order of increasing partial atomic energy. <sup>c</sup>  $\Delta e_i$  is the change in partial atomic energy on going from the orthorhombic structure to the structure studied here.

lifted, and the two groups are in structurally different environments (Figure 2b,c).

For group I, the  $\Delta e_i$ 's of C9 and C19 are rather small, as is the  $\Delta e_i$  for Cl 26 (except for the 6-9 potential). Thus, the energetic environment of these atoms changes only slightly between the orthorhombic structure and the one treated here. Note that Cl is the largest single contributor in both the triclinic and orthorhombic structures. Cl 26 is the largest contributor here as well but the *change* in its energetic environment is minimal. However, the energy of Cl 16 increases significantly over the orthorhombic structure; thus, the energetic environment of the two chlorines is not identical in the  $P2_1$  structure. This is expected since disorder is not observed in this structure.

The previous observation of the energetic equivalence of the Cl environments in the  $P\bar{1}$  and  $Pccn$  structures, in spite of their crystallographic differences, is apparently a result of the demands of the chlorine atom. Since in reality these are  $\text{CH}_3$  groups in the true  $P2_1$  structure this requirement for energetic equivalence is lifted. This may well be one of the reasons that the dichloro compound does not pack in this structure. (Both the 6-12 and 6-exp potentials indicate that the energetic environment of this region is less stable in the ordered structure while the 6-9 indicates that the environments are the same ( $\Delta e_i = 0.38, 0.53, 0.06$  kcal/mol, respectively).<sup>14</sup> (This is the only case where all three potentials do not yield identical trends).

For group II, C4 shows a large decrease in energy, C2 a large increase. The overall contribution of the group is an increase in energy over the orthorhombic form of 0.54, 0.83, and 1.13 kcal/mol for the three potentials.

For group III, all carbons exhibit an increase in energy, as does the group as a whole (0.69, 0.57, 1.27 kcal/mol). However, hydrogens H12, H14, and H15 decrease significantly in energy. One of the largest changes is for H14, which had a positive partial atomic energy in both the triclinic and ortho-

rhombic cases but is now negative in this structure.

For group IV, the individual  $\Delta e_i$ 's are consistently smaller than for the aniline ring (group III) and the sums (-0.07, -0.14, -0.50 kcal/mol) are much smaller as well. The correspondence between the partial energies of the atoms in this group for this crystal structure and the orthorhombic one is remarkable and serves as a measure of the reliability of this type of approach for analyzing the energetics of crystal packing.

Thus, overall, the environment of Cl 16 changes by going to higher energy and the aniline ring and the bridge atoms as groups contribute as well to the overall increase in crystal energy over the orthorhombic structure. On the other hand, the benzylidene ring is in the same energy environment in the two structures. The molecular energy is lower here since the molecule approaches the conformation of minimal energy.<sup>4,5</sup>

It is of interest to focus on the largest, individual,  $\Delta e_i$ 's which we have italicized in Table III. If we sum these we obtain a net change of (1.38, 1.23, 1.66 kcal/mol) compared to a net change for all atoms of (1.55, 1.68, 1.50 kcal/mol). Thus, the environmental changes for these nine atoms alone (out of 25) can very nearly account for the difference between the orthorhombic structure and this hypothetical one. Note that all of these contributions, save C2, come from the aniline ring (including Cl 16), rather than the benzylidene ring, and we reach the same conclusion as in the analysis made by groups. The difference in environment of the aniline and benzylidene rings may be seen in Figures 2b and 2c, in which the structures have been plotted on the plane of the benzylidene and aniline rings, respectively.

In summary we have demonstrated again that the use of partial atomic energies in analyzing changes in molecular environments in crystals is a valid and useful approach, even when the energy differences involved are quite small. Our conclusions reached earlier for disordered crystals<sup>2a</sup> are ap-

plicable as well to ordered ones and the conclusions drawn from such an analysis are not dependent on the potential chosen, as long as a reasonable function is employed.

**Acknowledgment.** We are grateful to Ms. Pnina Dauber for carrying out many of the calculations presented here. This work was supported in part by a grant (to J.B.) from the Israel Academy of Science.

## References and Notes

- (1) (a) Weizmann Institute of Science. (b) University of Illinois. Permanent address: Chemistry Department, Ben-Gurion University of the Negev, Beersheva, Israel.
- (2) (a) J. Bernstein and A. T. Hagler, *J. Am. Chem. Soc.*, **100**, 673 (1978); (b) J. Bernstein and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 951 (1972).
- (3) J. Bernstein and I. Izak, *J. Chem. Soc., Perkin Trans. 2*, 429 (1976).
- (4) H.-B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, **54**, 1255 (1971); (b) R. Cimraglia and J. Tomasi, *J. Am. Chem. Soc.*, **99**, 1135 (1977); (c) J. Bernstein and A. T. Hagler, unpublished results.
- (5) T. Bally, E. Haselbach, S. Lanijova, F. Marscher, and M. Rossi, *Helv. Chim. Acta*, **59**, 486 (1976).
- (6) (a) J. Bernstein, I. Bar, and A. Christensen, *Acta Crystallogr., Sect. B*, **32**, 1609 (1976); (b) I. Bar and J. Bernstein, *ibid.*, **33**, 1738 (1977); (c) unpublished results.
- (7) J. Bernstein, unpublished results.
- (8) (a) A. T. Hagler and S. Lifson, *J. Am. Chem. Soc.*, **96**, 5327 (1974); (b) A. T. Hagler, L. Leiserowitz, and M. Tuval, *ibid.*, **98**, 4600 (1976); (c) A. T. Hagler and S. Lifson, *Acta Crystallogr., Sect. B*, **30**, 1336 (1974); (d) A. T. Hagler, E. Huler, and S. Lifson, *J. Am. Chem. Soc.*, **96**, 5319 (1974).
- (9) D. E. Williams, *Acta Crystallogr., Sect. A*, **30**, 71 (1974).
- (10) O. Kennard et al., Ed., "Molecular Structures and Dimensions", N. V. A. Oosthoek's Uitgevers Mij, Utrecht, 1972, pp S2-S3.
- (11) E. Giglio, *Nature (London)*, **222**, 339 (1969).
- (12) A. T. Kitaigorodskii, *Adv. Struct. Res. Diff. Methods*, **3**, 225 (1970).
- (13) A. T. Hagler and L. Leiserowitz, "On the Amide Hydrogen Bond and the Anomalous Packing of Adipamide", submitted for publication.
- (14) Subsequent listings of energy contributions are given for the three potentials in the same order.

# Six Coordination in High-Spin Ferric Porphyrins. A New Structural Type and Models for Aquomethemoglobin

Toshio Mashiko,<sup>1</sup> Margaret E. Kastner,<sup>2</sup> K. Spartalian,<sup>3</sup> W. Robert Scheidt,\*<sup>2</sup>  
and Christopher A. Reed\*<sup>1</sup>

Contribution from the Departments of Chemistry, University of Southern California, Los Angeles, California 90007, and University of Notre Dame, Notre Dame, Indiana 46556, and the Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802. Received March 20, 1978

**Abstract:** The synthesis and definitive characterization of the first examples of six-coordinate high-spin ferric porphyrin complexes are reported. Perchlorato(tetraphenylporphyrinato)iron(III) reacts with various weak field ligands L (sulfoxides, dimethylformamide, triphenylphosphine oxide, pyridine *N*-oxide) to give isolable crystalline derivatives [FeL<sub>2</sub>(tetraphenylporphyrinato)]ClO<sub>4</sub>. Magnetic, Mössbauer, ESR, and structural data support a high-spin state assignment and certain properties parallel those of aquomethemoglobin. The crystal structure of bis(tetramethylene sulfoxide)(tetraphenylporphyrinato)iron(III) perchlorate, FeN<sub>4</sub>C<sub>52</sub>H<sub>44</sub>S<sub>2</sub>O<sub>6</sub>Cl, has been determined: space group *P* $\bar{1}$ ; *Z* = 2; *a* = 14.003 (5), *b* = 15.246 (5), *c* = 12.108 (3) Å;  $\alpha$  = 113.20 (2),  $\beta$  = 89.24 (2),  $\gamma$  = 76.67 (4)°; 7586 reflections, *Mo K* $\alpha$ ; *R*<sub>1</sub> = 0.076, *R*<sub>2</sub> = 0.089 with final data/parameter ratio of 13.2. In contrast to all other known high-spin ferric porphyrins the iron atom is precisely located in the plane of an expanded porphyrin core with mean Fe-N 2.045 (5) Å. The axial tetramethylene sulfoxide ligands are O-bound with Fe-O 2.069 (3) and 2.087 (3) Å, respectively, in the two independent half-molecules of the unit cell.

A curious feature of heme chemistry is that while *six* coordination is known in high-spin ferric hemoproteins it has been frequently ignored, largely because decades of ferric porphyrin isolation has yielded only *five*-coordinate high-spin derivatives.<sup>4</sup> Illustrative of this point is the contrast of six coordination in aquo- and fluoromethemoglobin with five coordination in complexes such as  $\mu$ -oxo derivatives, hemin fluoride, FeCl(TPP),<sup>5</sup> and numerous others.<sup>6-8</sup> The five-coordinate derivatives invariably have considerable iron atom displacements from the mean plane of the porphyrin<sup>7</sup> and this has led to the converse belief that high-spin states imply five coordination. While this remains a reasonable belief for *ferrous* porphyrins (and ferrous hemoproteins) the first experimental evidence that this might not be true for *ferric* porphyrins came with the very recently reported structure of [Fe(H<sub>2</sub>O)<sub>2</sub>(TPP)]ClO<sub>4</sub>.<sup>9</sup> Also, metal ion size effects have been questioned in theoretical studies<sup>10,11</sup> which, with a certain degree of simplification, stress the importance of nonbonding repulsions of the axial ligands with the porphyrin core rather than the

mismatch of large metal ions with the restricted porphyrin hole size. We report herein the first definitively characterized examples of six-coordinate high-spin ferric porphyrins. Although rather abiological in the identity of their axial ligands, certain properties of these complexes model high-spin methemoglobin derivatives. The X-ray crystal structure of one complex, [Fe(TMSO)<sub>2</sub>(TPP)]ClO<sub>4</sub>, reveals an in-plane iron atom and emphasizes that considerable caution must be exercised in assigning the stereochemistry of ferric porphyrin complexes and ferric hemoproteins from magnetic properties. Concurrent with our synthetic and structural work NMR studies have shown that six coordination exists in dimethyl sulfoxide solutions of high-spin ferric porphyrins.<sup>12</sup> Prior to the aforementioned [Fe(H<sub>2</sub>O)<sub>2</sub>(TPP)]ClO<sub>4</sub> all characterized six-coordinate ferric porphyrins have been *low* spin having axial ligands of moderate to high field strength (e.g., imidazole,<sup>13</sup> 2-methylimidazole,<sup>14</sup> cyanide,<sup>15</sup> thiolates,<sup>8</sup> thiol,<sup>16</sup> halides, pseudo-halides, thioethers,<sup>17</sup> and some combinations thereof).

The characterization of six-coordinate synthetic models for