(46) R. K. Boeckmann, *J. Org. Chem.*, **38**, 4450 (1973).

(47) (a) R. Deghneghi, C. Revesz, and R. Gaudry, *J. Med. Chem.*, **6**, 301 (1963); (b) M. J. Weiss, R. E. Schaub, G. R. Allen, J. F. Poletto, C. Pidacks, R. B. Conrow, and C. J. Casica, *Tetrahedron*, **20**, 357 (1964); (c) J. Cairns, C. L. Hewett, R. T. Logan, G. McGarry, D. F. M. Stevenson, and G. F. Woods, *J. Chem. Soc., Perkin Trans. 1*, 1558 (1976).

(48) (a) Cf. G. Stoke and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963); (b) W. E. Harvey and D. S. Tarbell, *J. Org. Chem.*, **32**, 1679 (1967); (c) see, for example, the use of 5-phenyl-2-lithiomethyloxazolines in asymmetric syntheses: A. I. Meyers and E. D. Mihelich, *Angew. Chem., Int. Ed. Engl.*, **15**, 270 (1976).

(49) (a) J. H. Dygos and L. J. Chinn, *J. Org. Chem.*, **38**, 4319 (1973); (b) A. Horeau, E. Lothioy, and J. P. Guetté, *C. R. Acad. Sci., Ser. C*, **269**, 558 (1969).

(50) For Friedel-Crafts cyclization of AB-aromatic 9,11-secosteroids into the corresponding 11-keto 19-norsteroids see (a) A. J. Birch and G. S. R. Subba Rao, *Aust. J. Chem.*, **23**, 547 (1970); (b) G. Eglinton, J. C. Nevenzel, A. I. Scott, and M. S. Newman, *J. Am. Chem. Soc.*, **78**, 2331 (1956).

(51) G. H. Posner and C. M. Lentz, *Tetrahedron Lett.*, 3769 (1978).

(52) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971).

(53) R. Watson and A. Eastman, *J. Organomet. Chem.*, **9**, 165 (1966).

(54) G. M. Whitesides, Jr., W. Fisher, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, **91**, 4877 (1969).

(55) H. O. House, C. Y. Chu, J. M. Wilkins, and M. J. Umen, *J. Org. Chem.*, **40**, 1460 (1975).

(56) Prepared from *p*-bromoanisole and magnesium turnings in THF.

(57) We have found that slow addition of the Grignard reagent to a vigorously stirred mixture of the enone and the copper catalyst gave optimum results.

(58) Prepared from *n*-butyllithium and diisopropylamine.

(59) H. O. House, R. A. Auerback, M. Gall, and N. P. Peet, *J. Org. Chem.*, **38**, 514 (1973).

(60) R. A. Olofson, K. D. Lotts, and G. N. Barber, *Tetrahedron Lett.*, 3381 (1976).

(61) I. Irie, T. Suzuki, S. Ito, and Kurosawa, *Tetrahedron Lett.*, 3187 (1967).

(62) G. L. Chetty, *Tetrahedron Lett.*, 75 (1964).

(63) Methylcopper was prepared by the addition of 0.2 mmol of methyllithium to 0.2 mmol of cuprous iodide in 1.0 mL of anhydrous THF. Methylcopper appears as a bright yellow precipitate.

(64) A. Ajima, H. Mizuno, and K. Takahashi, *Chem. Pharm. Bull.*, **20**, 197 (1972).

(65) D. J. Goldsmith and L. Sakano, *Tetrahedron Lett.*, 2857 (1974).

(66) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).

Hydrogen Bonding in N-Substituted Amino Acids. Crystal Structure of the *N,N*-Diethyl-β-alanine–Benzene Inclusion Compound

M. A. Peterson, H. Hope, and C. P. Nash*

Contribution from the Department of Chemistry, University of California, Davis, California 95616.

Received August 15, 1978

Abstract: Supersaturated solutions of *N,N*-diethyl-β-alanine (NNDEBA) in benzene deposit orthorhombic crystals, space group *Pbcm*, having four molecules of NNDEBA and four molecules of benzene in a unit cell with dimensions (160 K) a = 5.491 (1), b = 13.426 (3), c = 17.766 (6) Å. The amino acid molecules form hydrogen-bonded chains of zwitterions parallel to the b axis of the crystal. The molecules are situated on a crystallographic mirror plane, but the hydrogen-bonded oxygen appears to undergo large amplitude motion, so that the oxygen is ±0.46 Å out of the mirror plane most of the time. This motion leads to a mean N–O distance of 2.66 (2) Å. The in-plane N–O distance is computed to be 2.594 (5) Å. The zwitterion chains stack to form sheets parallel to the ab plane, with the ethyl groups nearly perpendicular to the sheets. Such a packing forms channels in which the benzene molecules are found. Electrostatic calculations in the point dipole approximation show that dipole–dipole interactions greatly stabilize an ab plane, but do not contribute significantly to the binding between adjacent ab planes.

Previous studies[1,2] have established that in aprotic solvents the equilibrium constant for the tautomeric equilibrium between the classical and zwitterionic forms of N,N-dialkylated amino acids is solvent dependent. Current work in our laboratory is concerned with the observation that some of these compounds also exhibit proton transfer in the solid state,[3] whereas others do not.

N,N-Disubstituted amino acids have only a single functional proton, so one might anticipate that the crystal of each such compound would contain only one kind of N–H–O hydrogen bonding configuration. If this expectation is realized in practice, structural, spectroscopic, and thermodynamic studies of this class of compounds could provide experimental results that would bear on the nature of the hydrogen-bond potential function.

The present paper reports the crystal structure of the benzene inclusion compound of *N,N*-diethyl-β-alanine (NNDEBA), $(C_2H_5)_2N(CH_2)_2COOH$, in which there occurs a single kind of very short NH–O hydrogen bond.

Experimental Section

Single-Crystal X-ray Investigation. NNDEBA was synthesized by the general procedure previously described.[1] A single crystal of NNDEBA–benzene was cut from a large, polycrystalline mass that formed when a sealed vial that originally contained a supersaturated solution of NNDEBA in benzene stood undisturbed for several years. The crystal, with dimensions 0.3 × 0.3 × 0.3 mm, was covered with the resin portion of an epoxy cement to prevent it from disintegrating. It was mounted onto a Syntex P2_1 four-circle diffractometer system fitted with a copper-target X-ray tube and a graphite monochromator. A stream of cold nitrogen gas maintained the crystal temperature at about 160 K. Information derived from a rotation photograph taken about a randomly oriented axis was used in the Syntex autoindexing and least-squares programs to determine the cell dimensions. Axial photographs indicated that the cell was orthorhombic. Seventeen reflections in the range $17° \leqslant 2\theta \leqslant 70°$ were used in the determination of cell and orientation parameters. The cell dimensions (160 K), obtained using λ Cu Kα = 1.54178 Å, are a = 5.491 (1), b = 13.426 (3), and c = 17.766 (6) Å. The structure is described in space group *Pbcm* (vide infra).

The crystal density, measured by flotation at room temperature, is 1.10 g cm^{-3}, whereas the density of a crystal having just four NNDEBA molecules in the unit cell would be 0.736 g cm^{-3}. The higher observed density suggests that the crystal also contains benzene. A unit cell with the cited dimensions containing four molecules of the amino acid and four molecules of benzene would have a density of 1.13 g cm^{-3}.

A set of intensity data was obtained using θ–2θ scan with scan speeds varying between 2 and 60 deg min^{-1} for $2\theta < 130°$. The P2_1 diffractometer scans in steps of about 0.01°. Stationary background intensities were measured at each end of the scan. The peaks were scanned from $[2\theta(\alpha_1) - 1.1]°$ to $[2\theta(\alpha_2) + 1.1]°$ employing a total background counting time equal to half the counting time for the scan.

0002-7863/79/1501-0946$01.00/0

Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations[b]

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.4903 (8)	0.5710 (3)	0.2500	2.2 (2)	1.5 (2)	4.9 (2)	−0.1 (1)	0.0	0.0
C(2)	0.3140 (8)	0.4830 (3)	0.2500	2.1 (2)	1.3 (2)	7.2 (3)	0.0 (1)	0.0	0.0
C(3)	0.4424 (7)	0.3856 (3)	0.2500	1.8 (2)	1.3 (1)	4.4 (2)	−0.1 (1)	0.0	0.0
N(4)	0.2813 (5)	02954 (2)	0.2500	1.8 (1)	1.0 (1)	3.3 (1)	−0.2 (1)	0.0	0.0
C(5)	0.1261 (6)	0.2863 (2)	0.1821 (2)	4.8 (2)	2.4 (1)	2.5 (1)	−1.6 (1)	−0.5 (1)	0.1 (1)
C(6)	0.2678 (15)	0.2815 (3)	0.1103 (3)	14.6 (5)	3.6 (2)	3.6 (2)	−3.1 (3)	3.0 (3)	−0.6 (2)
O(7)	0.7098 (5)	0.5558 (2)	0.2500	1.8 (1)	1.9 (1)	4.5 (2)	−0.2 (1)	0.0	0.0
O(8)	0.3912 (6)	0.6563 (2)	0.2500	2.1 (1)	1.1 (1)	16.6 (4)	−0.0 (1)	0.0	0.0
C(9)	0.7999 (9)	0.0527 (4)	−0.0071 (5)	4.5 (2)	5.0 (2)	17.9 (6)	0.4 (2)	−3.8 (3)	−2.5 (3)
C(10)	0.9271 (13)	0.0607 (4)	0.0549 (3)	9.4 (4)	5.5 (2)	5.7 (2)	−3.4 (3)	3.5 (3)	−1.9 (2)
C(11)	1.1286 (13)	0.0087 (4)	0.0636 (3)	11.7 (4)	5.8 (3)	6.4 (3)	−5.6 (3)	−6.8 (3)	3.4 (2)
H(2)	0.220 (7)	0.492 (3)	0.209 (2)	6.9 (12)					
H(3)	0.555 (6)	0.381 (2)	0.207 (2)	4.5 (8)					
H(4)	0.402 (11)	0.237 (4)	0.250	7.0 (15)					
H(51)	0.012 (7)	0.344 (3)	0.181 (2)	5.6 (9)					
H(52)	0.037 (6)	0.223 (2)	0.188 (2)	3.9 (7)					
H(61)	0.184 (9)	0.267 (4)	0.068 (3)	8.2 (15)					
H(62)	0.408 (8)	0.232 (4)	0.117 (3)	7.8 (14)					
H(63)	0.347 (7)	0.339 (3)	0.099 (2)	5.4 (9)					
H(9)	0.659 (11)	0.096 (5)	−0.025 (3)	11.5 (17)					
H(10)	0.859 (11)	0.108 (5)	0.100 (4)	12.1 (17)					
H(11)	1.199 (9)	0.014 (4)	0.107 (3)	8.8 (14)					

[a] The anisotropic thermal parameters are of the form $\exp[-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)/4]$. [b] Numbers in parentheses here and throughout the paper are estimated standard deviations in the last significant digits.

The intensities of two check reflections were measured after every 100 reflections; no systematic drift was seen.

Within the given 2θ range there should be 1349 reflections, but systematic absences occurred for the reflections $h0l, l = 2n + 1$, and $0kl, k = 2n + 1$, thereby reducing the number of observable reflections to 1157. Of these, 1040 had intensities greater than $3\sigma(I_{\text{net}})$ and were used in refinements. The data were corrected for Lorentz and polarization factors, but no absorption corrections were applied.

Spectroscopic Techniques. An infrared spectrum of the solid was taken with a Beckman Model IR-12 spectrophotometer. The spectroscopic sample was prepared in a glovebag saturated with benzene vapor. A few fragments of the crystal were crushed between two sodium chloride plates. These were then mounted in a holder designed to thread onto a brass rod that was machined to fit into a glass standard-taper joint sealed into the side of an infrared gas cell fitted with demountable sodium chloride windows.

The cell was assembled with a tray of liquid benzene inside in order to maintain a benzene atmosphere, and thus prevent it from escaping from the solid. By rotating the brass rod the sample could be turned upward out of the beam, and hence the background spectrum of the benzene vapor in the cell could also be recorded.

Structure Determination. Direct methods were used to solve the structure. Calculations were done at the UCD Computer Center on a Burroughs B7600 machine using programs developed or modified in this laboratory.

The cited systematic absences are consistent with the space groups *Pbcm* and $Pbc2_1$. A Wilson[4] plot was used to obtain an overall temperature factor and to produce normalized structure factors. The distribution of the structure factors indicated a centrosymmetric cell,[5] and hence the space group *Pbcm*. The sign-predicting program of Long,[6] which is based on Sayre's equation,[7] was used to develop 16 sets of signs for the 152 reflections with $E \geqslant 1.5$. The set with the highest consistency index (0.832) was used to produce an E map. All 11 of the nonhydrogen atoms in the asymmetric unit were found. Four cycles of full-matrix least-squares refinements using isotropic temperature factors brought $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ to 0.28. The least-squares program minimizes the weighted sum of the residuals $(\Sigma w(|F_o| - |F_c|)^2)$. The weighting factor, w, initially was defined in terms of the Hughes weighting scheme.[8] These calculations resulted in very large isotropic temperature factors for the benzene carbons and the methyl carbon, with slow convergence.

Next, anisotropic temperature factors were invoked and several cycles of block-diagonal least-squares refinement were calculated. The blocks were derived from the scale factor, a four-atom fragment consisting of the carboxylate group and the adjacent methylene carbon, a four-atom set composed of the benzene and methyl carbons, and a set that contained the remaining three nonhydrogen atoms. The resulting R was 0.15.

All the hydrogen atom positions were then determined from a difference Fourier map. After isotropic temperature factors were assigned to the hydrogen atoms, full-matrix least-squares refinement using $1/\sigma^2(F)$ weights brought R to convergence at 0.080.

In order to confirm the choice of space group, the structure was also refined in the alternative space group, $Pbc2_1$. The final parameters determined for the structure in *Pbcm* were used as initial parameters for these calculations. Because of the loss of symmetry, positions had to be specified for all the atoms in one molecule of NNDEBA and one molecule of benzene. Throughout the refinements the z coordinate of atom C(1) was held fixed. Anisotropic thermal parameters were employed only for the benzene and methyl carbon atoms. Full-matrix least-squares refinements of the nonhydrogen atoms, with the hydrogen atoms included in the structure factor calculations, gave a final R value of 0.24. This result clearly rules out the space group $Pbc2_1$.

In the structure obtained in *Pbcm*, the thermal parameters for the oxygen (O(8)) which is hydrogen bonded to nitrogen (N(4)) indicate a large amplitude (±0.46 Å) motion normal to the mirror plane. It is conceivable that an improved description of this structure would result from a model that employs two half-oxygens displaced from the mirror plane. We therefore refined the structure according to this model, using isotropic temperature factors for the half-oxygens. Full-matrix refinement converged with an R index of 0.086. In the resulting structure several C–H distances are clearly aberrant, and, moreover, an application of Hamilton's significance test[9] shows that it is more than 99.5% certain that the R values derived from the two alternative descriptions of the structure are different. For these reasons we believe that the "ordered" description provides a mathematically better model. While there may be some barrier to the motion of the oxygen across the mirror plane, it is evidently small enough to rule out the possibility of static disorder (vide infra). The structure will be discussed on the basis of the parameters from the "ordered" model, but it will also be shown that when thermal motion is taken into account both models give virtually the same mean N–O distance in the hydrogen bond.

Results and Discussion

The final atomic parameters are given in Table I. Figure 1 shows the molecular conformation of NNDEBA in the crystal, together with the scheme by which its atoms are numbered. Figure 2 shows the stacking pattern of the benzene molecules

Table II. Bond Distances[a] (Å) and Bond Angles[a] (deg)

intramolecular		intermolecular		intramolecular		intermolecular	
C(1)-C(2)	1.527 (6)	O(8)-N(4)[c]	2.594 (5)	O(7)-C(1)-O(8)	125.1 (4)	O(8)-N(4)[c]-C(5)[c]	109.8 (2)
C(2)-C(3)	1.486 (5)	O(8)-H(4)[c]	1.57 (6)	C(2)-C(1)-O(7)	119.7 (3)	N(4)[c]-O(8)-C(1)	110.7 (3)
C(3)-N(4)	1.499 (5)			C(2)-C(1)-O(8)	115.2 (4)	N(4)[c]—H(4)[c]-O(8)	174 (6)
N(4)-C(5)	1.482 (4)			C(3)-C(2)-C(1)	112.3 (3)		
C(5)-C(6)	1.495 (7)			N(4)-C(3)-C(2)	115.5 (3)		
C(1)-O(7)	1.223 (5)			C(5)-N(4)-C(3)	114.0 (2)		
C(1)-O(8)	1.267 (5)			C(6)-C(5)-N(4)	113.5 (4)		
C(9)-C(10)	1.309 (10)			C(11)[b]-C(9)-C(10)	121.2 (5)		
C(10)-C(11)	1.317 (9)			C(9)-C(10)-C(11)	120.2 (5)		
C(9)-C(11)[b]	1.357 (9)			C(10)-C(11)-C(9)[b]	118.5 (6)		
C(2)-H(2)	0.90 (4)			C(5)-N(4)-C(5)[d]	109.0 (3)		
C(3)-H(3)	0.99 (3)						
N(4)-H(4)	1.02 (6)						
C(5)-H(51)	1.00 (4)						
C(5)-H(52)	0.99 (3)						
C(6)-H(61)	0.90 (6)						
C(6)-H(62)	1.02 (5)						
C(6)-H(63)	0.92 (4)						
C(9)-H(9)	1.02 (6)						
C(10)-H(10)	1.09 (6)						
C(11)-H(11)	0.87 (6)						

[a] Not corrected for thermal motion. [b] Atom inverted through center of symmetry. [c] Atom at $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$. [d] Atom reflected through mirror plane.

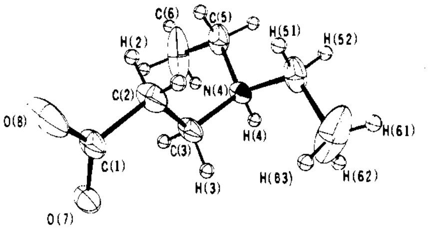

Figure 1. A drawing of the NNDEBA molecule showing the numbering scheme employed. The nonhydrogen atoms are drawn at their 50% probability levels. The hydrogen atoms are represented by 0.1 Å radius spheres.

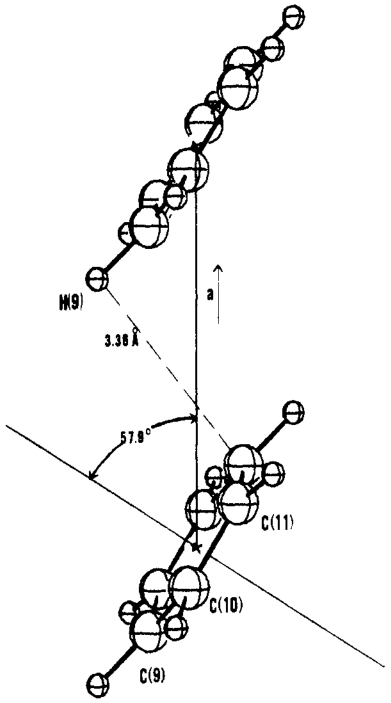

Figure 2. A detail of the stacking of the benzene molecules in the crystal showing the closest intermolecular contact, and also the atom numbering scheme employed. The carbon and hydrogen atoms are represented by 0.2 and 0.1 Å radius spheres, respectively.

in the crystal, and the atom designations. Bond distances and bond angles are listed in Table II.

In this crystal NNDEBA is in the zwitterionic form typical of virtually all amino acids in the solid state. This configuration is indicated both by the position of the functional hydrogen as inferred from the Fourier difference map and by the infrared spectrum of the solid, which shows a strong absorption at 1620 cm^{-1}. This absorption, typical of the carboxylate anion, is similar in frequency to those observed at 1604 and 1612 cm^{-1} for the sodium salts of *N,N*-diethyl-α-alanine and *N,N*-diethylglycine, respectively.[10]

There are significant differences between the structures of NNDEBA and its parent amino acid, β-alanine. In crystalline β-alanine the C-O bond lengths are equal within experimental error, the average bond length being 1.290 Å.[11] In β-alanine both oxygens participate in strong hydrogen bonding, whereas in NNDEBA hydrogen bonding occurs only with O(8). The C-O bond lengths in NNDEBA are the same as those in bis(*dl*-*N,N*-diethyl-α-alaninato)copper(II),[10] in which only one oxygen of each amino acid anion is bonded to the copper atom.

NNDEBA and β-alanine also differ in the respect that the dialkylamino and carboxyl groups of NNDEBA are in an anti configuration, whereas in β-alanine the amino and carboxyl groups adopt a syn configuration.

A stereoscopic packing diagram of the crystal of NNDEBA-benzene is shown in Figure 3. The backbones of the amino acid molecules form hydrogen-bonded chains parallel to the *b* axis of the crystal. Stacks of these chains form sheets parallel to the *ab* plane, with the ethyl groups nearly perpendicular to the sheets. Such a packing forms channels into which the benzene molecules stack as shown in Figure 2.

The benzene carbon atoms have large anisotropic temperature factors, indicative of a substantial libration about the molecular sixfold axis. A similar libration has been observed in crystalline benzene,[12,13] for which, at 138 K, an amplitude of ±2.5° has been reported.[12] In the present instance, the method of Cox et al.[13] yields the result that in the NNDEBA matrix at 160 K the benzene molecules have a mean amplitude of libration about the sixfold axis of ±10°. This observation, together with the fact that the benzene readily volatilizes at

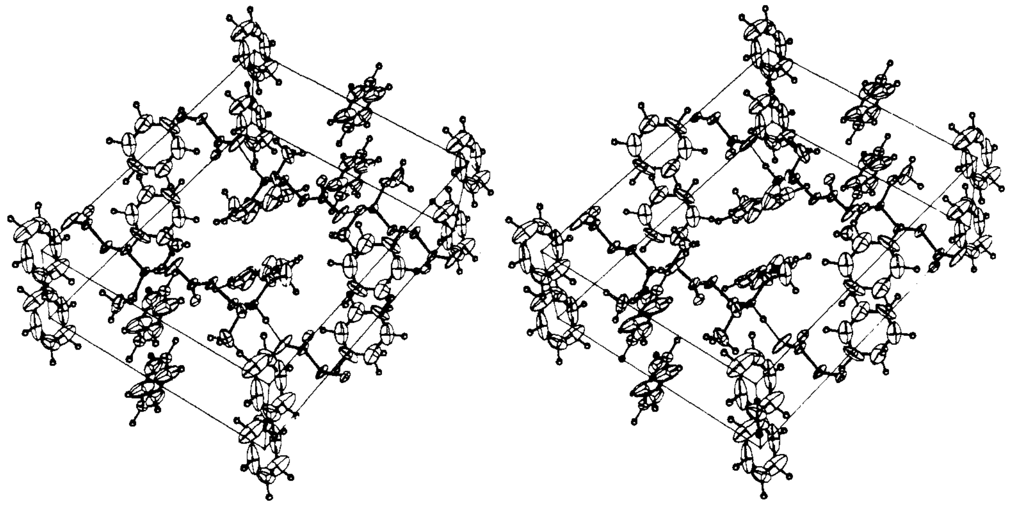

Figure 3. A stereoscopic drawing of the unit cell of the NNDEBA–benzene crystal. The nonhydrogen atoms are drawn at their 50% probability levels. Most of the hydrogen atoms have been omitted. Those included are represented by 0.1 Å radius spheres. Axes: *a* up, *b* left, *c* right.

room temperature, is evidence that it is weakly bound in the crystal.

Hydrogen Bonding. The configuration adopted by the NH^+-OOC^- hydrogen-bonded fragment in this crystal should closely approximate the ideal one for such a system. That is, there are no other interactions apparent elsewhere in the unit cell that would prevent the hydrogen-bonded groups from achieving a geometry dictated almost exclusively by the shape of the H-bond potential function. It should be emphasized, of course, that the potential function itself can be strongly influenced by the nature of the environment in which the hydrogen bond is embedded.[1,2,14–16]

In two recent papers Momany and co-workers have used crystal data to evaluate the parameters in a general one-dimensional analytic potential function for hydrogen bonds of several types.[17,18] According to these authors, the energy minimum in an NH^+-O^- hydrogen bond occurs when the H–O distance is 1.64 Å.[18] When atom O(8) is in the mirror plane the H(4)–O(8) distance is 1.57 Å, while at the root mean square O(8) displacement from the mirror plane the distance between these atoms is 1.63 Å. If the potential function of Momany et al. is directly applicable to the present system, we conclude that there are energy minima when O(8) is near its maximum observed displacement on either side of the mirror plane, with an energy barrier of 500 cal between them. A barrier of only $1.5kT$ is surely too small to permit static disorder in the crystal.

A consideration of N–O distances also supports our view that in this crystal the hydrogen bond length is at or near the minimum value possible for NH^+-O^- systems. Owing to the large temperature factor for atom O(8), the mean N–O separation will be larger than the value of 2.594 (5) Å computed from the positional parameters in Table I. Because the nitrogen and oxygen atoms are engaged in strong hydrogen bonding, their relative motion should be at least partially correlated.

Since the configuration in which N(4), H(4), and O(8) are all in the mirror plane appears to be that of a slight energy maximum, it is at least reasonable to suppose that the motions of the nitrogen and oxygen atoms will be in opposite directions relative to the mirror plane. The mean separation between them, corrected for thermal motion, should therefore lie between the maximum value and the value for noncorrelated motion, both of which we compute from the formulas of Busing and Levy.[19] For the "ordered" model of the crystal structure we thus find the mean N–O separation to lie in the range 2.65–2.69 Å.

The positional parameters for the "disordered" model of the crystal structure give a separation between N(4) and either of the half-oxygens of 2.615 (4) Å. When this distance is corrected for thermal motion in a similar fashion we find a mean separation in the range 2.64–2.66 Å. For comparison purposes, we shall assign a value of 2.66 (2) Å to the mean hydrogen-bond length in this crystal.

We have surveyed over 200 papers that report the structures of amino acids, simple peptides, and other substances in which amino groups or other nitrogen bases engage in NH–O hydrogen bonding, restricting our attention to those systems for which the authors report N–O distances having estimated standard deviations less than 0.02 Å. Out of a total of 405 such hydrogen-bond lengths, only 11 were found to have N–O distances of 2.70 Å or less. All of these involved a nitrogen atom bearing a formal positive charge. The shortest N–O distance found in the search was the value 2.60 (1) Å reported by Potter[20] for the hydrogen bond in 1,4-piperazine-γ,γ'-dibutyric acid at room temperature. The hydrogen bond in this crystal is nearly identical in all respects with the one in NNDEBA–benzene. When we compute a mean N–O distance from Potter's reported isotropic thermal parameters, we find it to lie in the range 2.64–2.68 Å.

The next-shortest N–O hydrogen-bonded distances, both of them also derived from structures determined at room temperature, were 2.660 (5) Å in chondrine[21] and 2.664 (5) Å in *l*-*N*-acetylhistidine monohydrate.[22] When these distances are corrected for thermal motion using the authors' reported anisotropic thermal parameters, mean-distance ranges of 2.70–2.73 and 2.69–2.70 Å, respectively, result. It is also noteworthy that in both of these structures the amplitude of the oxygen motion normal to the "uncorrected" N–O vector is approximately twice that of the nitrogen atom. The similar, but even more pronounced, behavior we find in NNDEBA–benzene at 160 K prompts us to suggest that the energy of short NH^+-O^- hydrogen bonds may be rather insensitive to small changes in the O–H–N angle. If this suggestion is correct, there might be a temperature range over which one would observe an *increase* in the length of one of the axes of the anisotropic thermal ellipsoid of an acceptor oxygen atom as the temperature is decreased. Physically speaking, the hydrogen bond might be able to "buckle" somewhat in response to thermal contraction of the rest of the crystal.

The results of our survey of hydrogen-bond lengths are summarized in Table III. Two correlations, which we simply present without further comment, are apparent. First, the N–O distance in a hydrogen bond is significantly shortened if the nitrogen atom has a formal positive charge. Also, for N^+-O^-

Table III. Average Nitrogen-Oxygen Distances[a] (Å) in NH-O Hydrogen Bonds Involving Nitrogen Bases

no. of H bonds to nitrogen	H-bond type			
	NH^+-O^-	NH^+-O	NH-O^-	NH-O
1	2.67	2.71	2.92	2.94
2	2.83	2.85	2.94	2.91
3	2.84	2.86		

[a] Not corrected for thermal motion.

and N^+-O hydrogen bonds a significantly shorter distance results if the nitrogen atom has only a single functional hydrogen. A correlation similar to this second one has also been noted very recently by Leiserowitz and Tuval[23] for the NH-O hydrogen bonds in amides. Here the average N-O separation was found to be 2.94 Å in primary amides and 2.85 Å in secondary amides.

Electrostatic Considerations. It is an instructive exercise to estimate the contribution to the lattice stability made by electrostatic interactions between the rather isolated NH^+-OOC^- dipoles. Because the closest approach distance of these units is about twice the separation of the positive and negative charge centers in the dipole, a point-dipole approximation should be reasonably satisfactory.[24]

The dipoles that are present in the crystal arise from proton transfer in intermolecular hydrogen bonds. There is little doubt that if the crystal were sublimed, the resulting gaseous monomers would have a classical rather than a zwitterionic structure.[2,25,26] Nevertheless, one can still choose the state of zero energy to be that of the hypothetical gas of monomeric zwitterions, each having a dipole moment equal to that of the dipole created between molecules in the crystal. Relative to this reference state, the dipole-dipole contribution to the lattice energy of the crystal is given by the equation[27]

$$E = \frac{1}{2}\sum_{n=2}^{\infty} \mu_1\mu_n \left[\frac{\mathbf{s}_1 \cdot \mathbf{s}_n}{|\mathbf{r}_{1n}|^3} - 3\frac{(\mathbf{s}_1 \cdot \mathbf{r}_{1n})(\mathbf{s}_n \cdot \mathbf{r}_{1n})}{|\mathbf{r}_{1n}|^5}\right] \qquad (1)$$

Here μ_1 and μ_n are the (equal) magnitudes of the central and nth dipole moments, $\mathbf{s}_1$ and $\mathbf{s}_n$ are unit vectors specifying the orientations of the central and nth dipole moment vectors, and $\mathbf{r}_{1n}$ is the vector joining the two dipoles in question. An outline of the planewise-summation method used to evaluate the lattice sum appears as part of the supplementary material for this paper.

For the sake of a numerical estimate, we take the dipole moment to be 12.0 D, based on a direct measurement of the dipole moment of the intramolecularly hydrogen-bonded, zwitterionic tautomer of *N,N*-dibutyl-β-alanine in methanol solution.[1] This value is only a lower bound for the dipole moment of the hydrogen-bonded fragment in the crystal. We shall find the internal field at a dipole site to be $\sim 2.5 \times 10^7$ V cm^{-1}, and the hydrogen bond can have a substantial polarizability.[14]

The direction of the dipole moment vector is assumed to be that of the line joining the nitrogen atom and the point in the mirror plane midway between the oxygen atoms in the carboxylate ion to which it is hydrogen bonded. The four dipole moment vectors in the unit cell are thus found to make angles with the *b* axis of the crystal of ±19.9° in the *ab* plane that contains the arbitrary origin, and 180 ± 19.9° in the *ab* plane half a *c* axis length away.

We find that, per mol of crystal, dipole-dipole interactions in the *ab* plane containing the origin contribute -14.544 kcal to the lattice energy. The two *ab* planes with $z = \pm 0.5$ contribute a total of -0.049 kcal to the lattice energy, while the two *ab* planes with $z = \pm 1$ together contribute $+3.5 \times 10^{-5}$ kcal to the lattice energy. From these results we conclude that, while dipole-dipole interactions are a major factor contributing to the stability of any given plane of the *ab* type, they alone cannot produce a stable three-dimensional structure with the observed lattice parameters. The electrostatic interaction energy between two adjacent planes is much smaller than thermal energy at room temperature. Thus van der Waals interactions, to which we presume the benzene molecules make a significant contribution, must be responsible for stabilizing the lattice in the *c*-axis direction.

Since the energy of a dipole in an external field is given by the scalar product of the electric field vector and the dipole moment vector, the interaction energy we compute for any plane of the *ab* type leads to a field strength at a dipole site of $(2.5 \times 10^7/\cos\theta)$ V cm^{-1}, where θ is the angle between the two vectors. The model calculations of Janoschek et al.[14] show very clearly that in external fields of this magnitude the hydrogen bond potential function is quite different from that calculated for the same system in field-free space. Thus a more sophisticated calculation of the stability of hydrogen-bonded lattices would have to take this effect into account in a self-consistent way.

Acknowledgments. We are grateful to the National Science Foundation for providing funds under Grant CHE 76-05569 toward the acquisition of the diffractometer used in this study. We also thank the UCD Computer Center for a grant of computing time. One of us (H.H.) acknowledges research support from the National Science Foundation.

Supplementary Material Available: A table listing observed and calculated structure factors and a supplementary section outlining the formalism used to obtain the lattice sum (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. A. Horsma and C. P. Nash, *J. Phys. Chem.*, **72**, 2351 (1968).
(2) J. W. O. Tam and C. P. Nash, *J. Phys. Chem.*, **76**, 4033 (1972).
(3) C. P. Nash, E. L. Pye, and D. B. Cook, *J. Phys. Chem.*, **67**, 1642 (1963).
(4) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).
(5) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).
(6) R. E. Long, Ph.D. Dissertation, University of California, Los Angeles, 1965.
(7) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1972).
(8) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).
(9) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(10) C. P. Nash and W. P. Schaefer, *J. Am. Chem. Soc.*, **91**, 1319 (1969).
(11) P. Jose and L. M. Pant, *Acta Crystallogr.*, **18**, 806 (1965).
(12) G. E. Bacon, N. A. Corey, and S. A. Wilson, *Proc. R. Soc. London, Ser. A*, **279**, 98 (1964).
(13) E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. R. Soc. London, Ser. A*, **247**, 1 (1958).
(14) R. Janoschek, E. G. Weidemann, H. Pfeiffer, and G. Zundel, *J. Am. Chem. Soc.*, **94**, 2387 (1972).
(15) E. G. Weidemann and G. Zundel, *Z. Naturforsch. A*, **28**, 236 (1973).
(16) N. Rosch and M. A. Ratner, *J. Chem. Phys.*, **61**, 3344 (1974).
(17) F. A. Momany, L. M. Carruthers, R. F. McGuire, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1595 (1974).
(18) F. A. Momany, L. M. Carruthers, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1621 (1974).
(19) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).
(20) R. Potter, *Acta Crystallogr.*, **20**, 54 (1966).
(21) K. S. Palmer, K. S. Lee, R. Y. Wong, and J. F. Carson, *Acta Crystallogr., Sect. B.*, **28**, 2789 (1972).
(22) T. J. Kistemacher, D. S. Hunt, and R. E. Marsh, *Acta Crystallogr., Sect. B.*, **28**, 3352 (1972).
(23) L. Leiserowitz and M. Tuval, *Acta Crystallogr., Sect. B*, 1230 (1978).
(24) C. J. F. Böttcher, "Theory of Electric Polarization", American Elsevier, New York, N.Y., 1952, p 7.
(25) Y. Grenie, J. C. Lassegues, and C. Garrigou-LaGrange, *J. Chem. Phys.*, **53**, 2980 (1970).
(26) A. Theoret, *Spectrochim. Acta, Part A*, **27**, 11 (1971).
(27) A. I. Kitaigorodsky, "Molecular Crystals and Molecules", Academic Press, New York, N.Y., 1973, p 144.