B_{11} to B_{33} computed by Grenville-Wells are $3\frac{1}{2}$ for nitrogen and almost 6 for oxygen. If anything, the electron density sections indicate, to us at least, that the anisotropy of the nitrogen atom is greater than that of the oxygen. Our analysis of our own (*h*0*l*) data indicates $B_{11} = 3{\cdot}65$ and $B_{33} = 1{\cdot}68$ for oxygen (at room temperature).

Our room temperature (least squares) results for B_{11} differ little from those of Worsham, Levy & Peterson. The B_{33} results, however, differ significantly. The Worsham, Levy & Peterson results are consistently lower than ours by as much as 50%.

Our low temperature measurements are useful in this connection. The temperature factors of all the atoms show a fairly uniform decrease of about 50% between room temperature and −140 °C. In this temperature range, the temperature factors are approximately proportional to the absolute temperatures. It is difficult to reconcile these findings with those reported by Worsham, Levy & Peterson. The *decrease* in our B_{33} terms between room temperature and −140 °C. was almost as large as the *total* room temperature values reported by Worsham, Levy & Peterson for the nitrogen and carbon atoms, and larger than the value reported for the oxygen atom. The B_{13} cross term for the nitrogen atom is very small and may be ignored.

The causes of these differences between the X-ray and the neutron diffraction results are not clear. It is well known that computed 'temperature factors' are particularly sensitive to the types of form factors assumed for the atom at rest. It may be that the differences reflect errors in the neutron, or the X-ray, atomic form factors. Possibly the three dimensional neutron diffraction analysis of urea reported under way at the Oak Ridge National Laboratories will clear up this point.

Table 5. *Urea*

Peak heights and central curvatures

	Peak heights (e.Å^{-2})		Central curvatures (e.Å^{-4})	
	Room temp.	−140 °C.	Room temp.	−140 °C.
C	9·9	14·4	A_{hh} 130	320
			A_{ll} 180	420
O	12·3	18·6	A_{hh} 130	370
			A_{ll} 170	430
N (*h*0*l*)	9·6	13·6	A_{hh} 60	140
			A_{ll} 120	250
N (*hk*0)	8·0	12·3	A_{hk} 40	130
			$A_{h\bar{k}}$ 70	185

Peak heights and curvatures of the 'heavy atom' peaks have been listed in Table 5. These were computed from the room temperature and the low temperature electron density maps. We have also included data for nitrogen obtained from (*hk*0) maps. These are of considerably lower reliability than the others because of overlap effects in this projection.

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The Magnetic Anisotropy and Electron Distribution in Succinimide

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A three-dimensional least-squares analysis of the crystal and molecular structure of succinimide is reported. The final discrepancy factor $R = 0{\cdot}091$ corresponds to average e.s.d.'s of 0·011 Å and 0·6° for the bond lengths and angles respectively. The principal molecular diamagnetic susceptibilities (−55·1, −45·1 and −41·6.10^{-6} c.g.s.e.m.u.), together with the inter- and intra-molecular bond lengths, are discussed in relation to the electron distribution in the molecule.

The refinement

A least-squares analysis of 30 (*hk*0), (0*kl*), (*h*0*l*) and (*hkl*) spacings gave the *Pbca* unit cell dimensions as,

$$a = 7{\cdot}537 \pm 0{\cdot}008,\ b = 9{\cdot}651 \pm 0{\cdot}011,\ c = 12{\cdot}938 \pm 0{\cdot}015\ \text{Å}\ .$$

The three-dimensional least-squares refinement, based on the two-dimensional analysis (Mason, 1956) and an isotropic temperature factor $B = 2{\cdot}6$ Å^2, reduced the residual factor

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$$R_{hkl} = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

for 705 reflexions from 0·26 to 0·091 in seven cycles. The observed structure factors, representing approximately 75% of these available within the Cu $K\alpha$ reflecting sphere, were based on visually estimated reflexion intensities on equi-inclination Weissenberg photographs. Four bipyramidal crystals of size ranging from $0{\cdot}05 \times 0{\cdot}07 \times 0{\cdot}07$ mm. to $0{\cdot}2 \times 0{\cdot}25 \times 0{\cdot}25$ mm. were subjected to shock heat treatment to minimize extinction effects; the crystal size and uniformity allow absorption effects to be ignored. McWeeny (1951) valence-state atomic scattering factors were used throughout a refinement scheme (Rollett, 1959) which simultaneously adjusts atomic co-ordinates and anisotropic vibration factors; the co-ordinates of the hydrogen atoms were refined in the last two cycles only, their thermal parameters being given values identical to those of the carbon and nitrogen atoms to which they are respectively bonded.

Four 'strong' reflexions apparently suffering from extinction ($|F_o| \approx 0{\cdot}75\,F_c$) and interfering with the proper adjustment of the scale and temperature factors were given zero weight after the second cycle, the remaining reflexions being assigned unit weights. The justification of unit weighting is not so obvious as in a number of two-dimensional analyses that have been carried out in this laboratory. In those instances, evidence that the errors were random, independent of $|F_o|$, came from extensive comparisons of data collected from a number of crystals in addition to the usual correlation of individual F_o and F_c's. It is possible that the present analysis is based on data which contain some systematic errors due to the inadequate integration of a number of reflexion intensities on equi-inclination Weissenberg photographs. It is unlikely that such errors, if present, would much affect the atomic co-ordinates, and therefore the bond lengths, or indeed would lead to serious underestimates of the standard deviations of these results. Rather, they would be assimilated by the vibration analysis so that the results of Table 2 may not be as significant as the usual statistical analysis would indicate. The main evidence for this argument comes from a comparison of the bond lengths and Debye factors in anthracene (Cruickshank, 1956; Sparks, 1958; Mason unpublished); the r.m.s. deviation in the bond lengths from these investigations is less than 0·01 Å whereas the Debye factors show systematic differences corresponding to changes in the average isotropic temperature factors of up to 1 Å^2. While these differences appear to be traceable to inadequate corrections of extinction effects, a similar result has been obtained in a three-dimensional analysis of 1·2:6·7 dibenzacridine (Mason, unpublished) through an initial systematic underestimate of a number of intensities, as a result of shape deformation, on upper-layer photographs of the Weissenberg type.

The tendency for oscillation in successive cycles of the least-squares was controlled by applying fractional shifts which varied from cycle to cycle in a way dependent upon the amplitude of the oscillation and the general progress of the refinement. Fractional shifts of the hydrogen co-ordinates were also used in a way that has been discussed elsewhere (Mason, 1960).

Results

The final atomic co-ordinates are listed in Table 1.

Table 1. *Succinimide*

Atomic co-ordinates

Atom	x/a	y/b	z/c
N_1	$0{\cdot}0468_6$	$0{\cdot}1131_9$	$0{\cdot}1053_9$
O_1	$0{\cdot}1967_1$	$0{\cdot}1205_1$	$0{\cdot}2609_5$
O_2	$-0{\cdot}1322_5$	$0{\cdot}1603_9$	$-0{\cdot}0344_2$
C_1	$0{\cdot}1028_6$	$0{\cdot}1772_6$	$0{\cdot}1942_0$
C_2	$-0{\cdot}0656_1$	$0{\cdot}1967_7$	$0{\cdot}0463_2$
C_3	$0{\cdot}0269_7$	$0{\cdot}3225_1$	$0{\cdot}1972_5$
C_4	$-0{\cdot}0776_5$	$0{\cdot}3349_7$	$0{\cdot}0986_1$
H_1	0·057	0·015	0·101
H_2	0·122	0·416	0·197
H_3	−0·028	0·343	0·251
H_4	−0·208	0·376	0·118
H_5	−0·035	0·429	0·050

Bond lengths and angles are shown in Fig. 1.

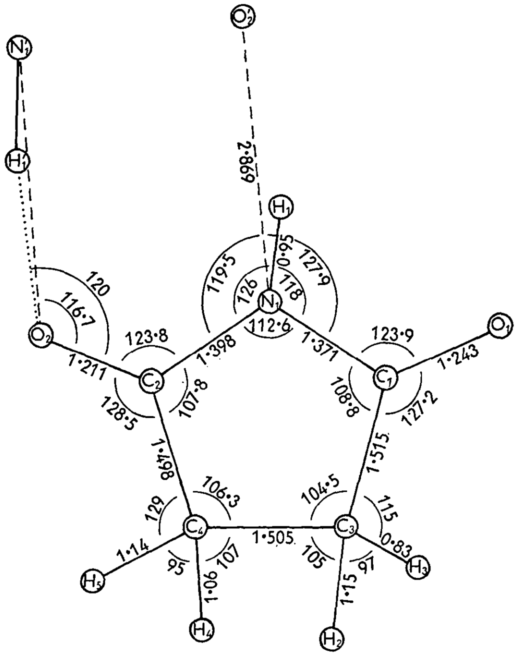


Fig. 1. Succinimide. Bond lengths and angles.

The thermal coefficients in the usual expression for the temperature factor,

$$T = \exp -\{b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl\}$$

are listed in Table 2.

Table 2. *Succinimide*

Atomic thermal parameters

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N_1	0·0058	0·0031	0·0028	0·0047	−0·0021	−0·0002
O_1	0·0141	0·0059	0·0050	0·0044	−0·0100	−0·0006
O_2	0·0204	0·0063	0·0028	0·0112	−0·0065	−0·0028
C_1	0·0065	0·0048	0·0021	−0·0042	−0·0011	−0·0008
C_2	0·0080	0·0041	0·0022	0·0034	−0·0001	0·0030
C_3	0·0077	0·0031	0·0030	0·0000	−0·0024	−0·0014
C_4	0·0153	0·0037	0·0024	0·0082	−0·0013	−0·0009

Discussion

The magnetic susceptibilities

The direction cosines of the principal molecular susceptibilities K_1, K_2 and K_3 (Mason, 1956) are now respectively

$$\begin{array}{l} 0{\cdot}8096,\ 0{\cdot}3090,\ -0{\cdot}4991 \\ 0{\cdot}5469,\ -0{\cdot}0830,\ 0{\cdot}8331 \\ -0{\cdot}2169,\ 0{\cdot}9470,\ 0{\cdot}2370\,. \end{array}$$

The calculated molecular susceptibilities are

$$\begin{aligned} K_1 &= -55{\cdot}1\,.\,10^{-6}\ \text{c.g.s.e.m.u.} \\ K_2 &= -41{\cdot}6\,.\,10^{-6}\ \text{c.g.s.e.m.u.} \\ K_3 &= -45{\cdot}1\,.\,10^{-6}\ \text{c.g.s.e.m.u.} \end{aligned}$$

and

$$\Delta K = K_1 - \tfrac{1}{2}(K_2 + K_3) = -11{\cdot}7\,.\,10^{-6}\ \text{c.g.s.e.m.u.}$$

The explanation of ΔK in conjugated π electron systems is usually given in terms of the peripheral ring currents, the magnetic effects of which can be calculated by the well-known London expression. The adequacy of this explanation is now doubtful, however, Hoarau (1956) suggesting that the magnetic anisotropy of a series of aromatic hydrocarbons could be better represented by the expression,

$$\Delta K_o = \Delta K_{\text{London}} + \Sigma \Delta k_\sigma + n \Delta k_\pi\,. \tag{1}$$

Δk_σ is now the anisotropy due to σ bond formation and $n\Delta k_\pi$ the sum of the anisotropies due to the *localised* π electrons. The effect of this last term is to increase the anisotropy, not through the usual enhancement of the out-of-plane susceptibility but by a decrease of the in-plane values. Its importance is made clear by an examination of the magnetic susceptibilities of anthracene and phenazine (Leela, 1958) which are listed in Table 3.

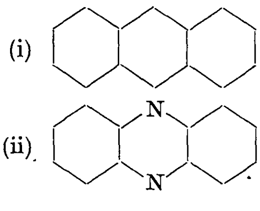
According to the London model, ΔK of Table 3 now results from the increase of K_3 with respect to K_1 and K_2; these last values should then be equal, within experimental error, to the sum of the atomic susceptibilities, $\Sigma\chi_{\text{at.}}$, which may be calculated from the magnetic constants based on simple saturated molecules. With $\chi_H = -2{\cdot}0$, $\chi_c = -7{\cdot}4$ and $\chi_N = -9{\cdot}0(.10^{-6}$ c.g.s.e.m.u.), we would also expect the K_1 and K_2's for anthracene and phenazine to be near-identical. In fact the equation,

$$\tfrac{1}{2}(K_1 + K_2)_o - \Sigma\chi_{\text{at.}} = n\alpha\,(\alpha \approx +3{\cdot}8\,.\,10^{-6}\ \text{c.g.s.e.m.u.}) \tag{2}$$

represents the observed susceptibilities not only in anthracene but in a considerable range of aromatic hydrocarbons (Hoarau, 1956). n is the number of trigonally hybridized carbon atoms and α a constitutive correction, expressing quantitatively the effect of Δk_π of equation (1) on the in-plane susceptibilities. It is therefore a measure of the change in magnetic properties accompanying a change in the symmetry of the atomic electron distribution. The differences between the in-plane susceptibilities of anthracene and phenazine indicate the increased electron localization in phenazine which is again reflected in the decrease of the effective delocalization term, $K_3 - \Sigma\chi_{\text{at.}}$ While an inspection of the ΔK's alone of anthracene and phenazine would therefore suggest similar electron distributions in these molecules, the actual susceptibilities point out the considerable perturbation of the electronic density on *aza*-substitution.

Table 3. *Molecular susceptibilities of anthracene and phenazine*

(units of -10^{-6} c.g.s.e.m.u.)



	(i)	(ii)
K_1	77·2	55·9
K_2	74·7	54·7
K_3	250·7	222·4
ΔK	174·7	167·1
$\frac{1}{2}(K_1+K_2)$	76·0	55·3
$\Sigma\chi_{\text{at.}}$	123·6	122·8
$K_3-\Sigma\chi_{\text{at.}}$	127·1	99·6

In succinimide, then, the average in-plane susceptibility may be written as,

$$\tfrac{1}{2}(K_1 + K_2)_o = 2\chi_{C(sp2)} + 2\chi_{C(sp3)} + 5\chi_H + \chi'_N + 2\chi'_O,$$

where the primed χ's refer to the modified atomic susceptibilities due to changes in the electron distribution on bond formation. The nitrogen of succinimide can reasonably be expected to have an atomic susceptibility nearer the value of $-9{\cdot}0\,.\,10^{-6}$ c.g.s.e.m.u. than that which can be calculated for phenazine ($\chi'_{N(\text{tertiary})} = +2{\cdot}0\,.\,10^{-6}$ c.g.s.e.m.u.). We then have,

$$\chi'_O = -1{\cdot}7\,.\,10^{-6}\ \text{c.g.s.e.m.u.}$$

Some check of the value of this calculation can be obtained from the data on *p*-benzoquinone (Lonsdale & Krishnan, 1936) where

$$\begin{gathered} K_1 = -24{\cdot}3,\ K_2 = -28{\cdot}7\ \text{ and} \\ K_3 = -67{\cdot}1\,.\,10^{-6}\ \text{c.g.s.e.m.u.} \\ \tfrac{1}{2}(K_1 + K_2)_o = -26{\cdot}5\,.\,10^{-6} = 6\chi_{C(sp2)} + 4\chi_H + 2\chi'_O\,, \end{gathered}$$

when

$$\chi_O = +1{\cdot}4\,.\,10^{-6}\ \text{c.g.s.e.m.u.}$$

Small changes in α would improve the agreement between these results which are based on the assumption that the anisotropy due to σ bonds is small. They both demonstrate, however, the large difference between χ_O' and χ_O ($-5{\cdot}3\,.\,10^{-6}$ c.g.s.e.m.u.).

The effective delocalization term in *p*-benzoquinone, as measured by $K_3 - \Sigma\chi_{\text{at.}}$, is only $-4{\cdot}1\,.\,10^{-6}$ c.g.s.e.m.u. as compared with the value of $-40\,.\,10^{-6}$ c.g.s.e.m.u. in benzene (one third of the anisotropy of benzene, $\Delta K = -60\,.\,10^{-6}$ c.g.s.e.m.u., originates from the Δk_π term). In succinimide, $K_{\text{max.}} - \Sigma\chi_{\text{at.}} = +4{\cdot}1\,.\,10^{-6}$ c.g.s.e.m.u.; the contribution of the ring currents is opposite in sign to that of benzene which is also the case for a number of other hetero-atom systems such as cyanuric trichloride ($K_{\text{max.}} - \Sigma\chi_{\text{at.}} = +5{\cdot}2\,.\,10^{-6}$ c.g.s.e.m.u., Lonsdale, 1936) and phosphonitrilic chloride where $\Delta K' = +12{\cdot}8\,.\,10^{-6}$ c.g.s.e.m.u. (Craig, Heffernan, Mason & Paddock, 1961). The explanation for this last result comes from an analysis of the symmetries and energies of the orbitals for which the quantum number $l = 0$. In the absence of a magnetic field these orbitals do not interact whereas a magnetic perturbation induces a mutual interaction of these orbitals, the net magnetic result of which is an overall paramagnetic contribution perpendicular to the ring plane.

In *p*-benzoquinone, the in-plane anisotropy is $-4{\cdot}4\,.\,10^{-6}$ c.g.s.e.m.u., the susceptibility along the direction $C=O$ ($-24{\cdot}3\,.\,10^{-6}$ c.g.s.e.m.u.) being greater than K_2($-28{\cdot}7\,.\,10^{-6}$ c.g.s.e.m.u.). In succinimide, K_2($-41{\cdot}6\,.\,10^{-6}$ c.g.s.e.m.u.) is nearer to the axis $C=O$ than K_3($-45{\cdot}1\,.\,10^{-6}$ c.g.s.e.m.u.). Using benzoquinone as a reference, an in-plane anisotropy of $-4{\cdot}4\cos^2 30°$, that is $-3{\cdot}3\,.\,10^{-6}$ c.g.s.e.m.u., is expected for succinimide; the observed anisotropy is $-3{\cdot}5\,.\,10^{-6}$ c.g.s.e.m.u.

It certainly seems clear that the interpretation of molecular susceptibilities of heteroatomic systems requires some care. An observed molecular anisotropy of the same sign as in benzene must not be taken as offering *a priori* evidence for delocalization phenomena. Nevertheless, the individual molecular susceptibilities may be more sensitive than bond lengths in giving details of the π electron distribution in the molecule.

Bond lengths

The average estimated standard deviation for the carbon–carbon, carbon–nitrogen and carbon–oxygen bond lengths of Fig. 1 is 0·011 Å; it is 0·11 Å for the C–H and N–H lengths. The e.s.d. for the bond angles is 0·6° for those angles involving carbon, nitrogen and oxygen and 5·0° for those involving the hydrogens.

The bond lengths C_2–C_4 (1·498 Å, e.s.d. 0·011 Å) and C_1–C_3 (1·515 Å, e.s.d. 0·012 Å) measure the separation between trigonally- and tetrahedrally-hybridized carbon atoms. The average observed bond length of 1·506 Å does not, contrary to suggestions contained in a number of recent analyses, indicate conjugative or hyperconjugative effects in the five-membered ring. The carbon–carbon single-bond length of 1·542 Å refers to the interatomic distance $C(sp^3)$–$C(sp^3)$. The atomic radius of carbon depends on the state of hybridization (Coulson, 1948); that of a trigonally hybridized carbon has been estimated at 0·735 Å (Craig & Mason, unpublished) so that the $C(sp^3)$–$C(sp^2)$ single-bond distance can be calculated, from the simple addition of radii, as 1·506 Å. The agreement with the observed average bond length is fortuitously good. On the other hand, the bond length of 1·505 Å for C_3–C_4 (e.s.d. 0·014 Å) is difficult to understand. Statistically, it appears significantly different from the normal single-bond length and the difference is too large to be accounted for by the effects of thermal vibrations in apparent bond shortening (Cox, Cruickshank & Smith, 1955) which a rough calculation suggests would be 0·007 Å. The result may possibly imply the presence of further unsuspected systematic errors in the X-ray data since alternative explanations involving hyperconjugative effects of the $-CH_2$ groups seem both improbable and unlikely to contribute a shortening of 0·03 Å.

The average $C=O$ and C–N distances of 1·227 Å and 1·385 Å respectively indicate the usual contribution of the $O^{-}\!-\!C=\overset{|\,+}{N}\!-$ structure to the ground-state configuration of the molecule. This contribution is not, however, sufficient to ensure complete planarity of the molecule; the least-squares equation to the normal of the plane continuing the carbon, nitrogen and oxygen atoms is

$$0{\cdot}8096x + 0{\cdot}3090y - 0{\cdot}4991z + 0{\cdot}1142 = 0$$

the atomic deviations from this plane being

N_1	+0·057 Å	C_1	+0·017 Å	H_1	−0·15 Å
O_1	−0·011	C_2	+0·002	H_2	+0·83
O_2	+0·008	C_3	−0·033	H_3	−0·65
		C_4	+0·003	H_4	−0·77
				H_5	+0·85

The e.s.d.'s of the bond lengths C_2–O_2 and C_1–O_1 are 0·009 Å and 0·010 Å, those for C_2–N and N–C_1 0·009 Å and 0·010 Å respectively, so that while the two $C=O$ and C–N distances are not significantly different, the results are of interest when related to other investigations of the dependence of intra-molecular bond lengths on the hydrogen-bonding environment of the molecule in the crystal. In succinimide, only one oxygen atom, O_2, is involved in hydrogen bonding and the C_2–O_2 bond length indicates a higher bond order than is the case for C_1–O_1. In L-glutamine (Cochran & Penfold, 1952) and L-leucyl–L-prolylglycine (Leung & Marsh, 1958) the $C=O$ group to which the larger number of hydrogen bonds are directed also appears shorter than the remaining groups in the molecule.

Table 4. *Succinimide*

Intermolecular bond lengths < 4 Å

Atoms in reference molecule	Atoms in neighbouring molecules	Intermolecular bond lengths
$C_1\ (x, y, z)$	$C_3\ (-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·828 Å
	$C_3\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·762
	$C_4\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·912
	$O_1\ (-\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·163
	$O_2\ (\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·273
	$O_2\ (-x, -y, -z)$	3·865
$C_2\ (x, y, z)$	$O_1\ (-\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·157
	$O_2\ (\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·549
	$O_2\ (-x, -y, -z)$	3·759
	$N_1\ (-x, -y, -z)$	3·581
	$N_1\ (-\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·968
$C_3\ (x, y, z)$	$C_4\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·984
	$O_1\ (-\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·208
	$O_2\ (\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·326
	$O_1\ (-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·377
	$O_1\ (\frac{1}{2}-x, \frac{1}{2}+y, z)$	3·645
	$O_2\ (x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·677
	$N_1\ (-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·834
$C_4\ (x, y, z)$	$O_1\ (-\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·237 Å
	$O_1\ (-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·421
	$O_2\ (\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·459
	$N_1\ (-\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·902
$N_1\ (x, y, z)$	$O_1\ (-\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·156
	$O_2\ (\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·386
	$N_1\ (-x, -y, -z)$	3·565
$O_1\ (x, y, z)$	$O_1\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·779
	$O_1\ (-\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·779
	$O_2\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	3·785
	$O_2\ (\frac{1}{2}+x, \frac{1}{2}-y, -z)$	3·837
$O_2\ (x, y, z)$	$O_2\ (-x, -y, -z)$	3·788
$H_1\ (x, y, z)$	$H_3\ (-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	2·54
	$H_1\ (-x, -y, -z)$	2·77
	$H_2\ (\frac{1}{2}-x, -\frac{1}{2}+y, z)$	2·88
	$H_4\ (-\frac{1}{2}-x, -\frac{1}{2}+y, z)$	2·99
$H_2\ (x, y, z)$	$H_4\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	2·76
	$H_3\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	2·82
$H_3\ (x, y, z)$	$H_4\ (\frac{1}{2}+x, y, \frac{1}{2}-z)$	2·99
$H_5\ (x, y, z)$	$H_5\ (-x, 1-y, -z)$	1·97

In a number of other analyses (see for example Pasternak *et al.*, 1954) this asymmetry dependence is reversed. As Leung & Marsh (1958) point out, the asymmetry may be, in part, an apparent one due to the different thermal vibrations of the oxygen atoms; in this respect, a proper correction would possibly need to consider the effects of intramolecular vibrations as well as the librational vibrations. It seems more useful at the moment to investigate the structure of some hydrogen-bonded crystals at low temperature before discussing possible mechanisms of intramolecular bond-length changes due to intermolecular forces.

The reference molecule at (x, y, z) is surrounded by fourteen neighbours. Apart from the N–H $\cdots$ O bond, whose geometry is shown in Fig. 1, the intermolecular forces are of the Van der Waals kind. Nearest neighbour distances are shown in Table 4.

The hydrogen–hydrogen separations are typical of the Van der Waals separations for a number of molecular crystals with the exception of H_5–H_5 $(-x, 1-y, -z)$; the intermolecular bond length here of 2 Å undoubtedly reflects the uncertainty in the location of this atom. Carbon–oxygen and nitrogen–oxygen interactions obviously play the major role in establishing the molecular orientation in the crystal; the carbon–oxygen distances range from about 3·2 Å, a non-hydrogen bonded N $\cdots$ O interaction of 3·156 Å probably indicating some electrostatic interaction $N^+ \cdots O^-$ over and above the usual dispersion forces and so on.

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