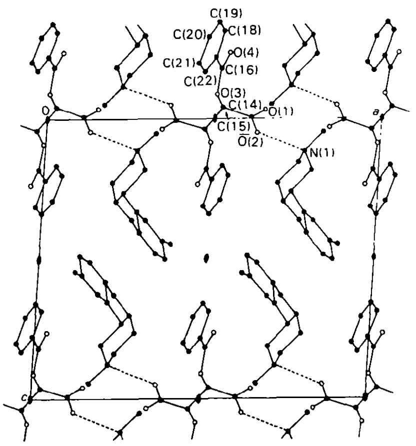

Fig. 1. The crystal structure projected along **b** and numbering scheme for *S,S*-DBTA. Hydrogen bonds are shown by broken lines.

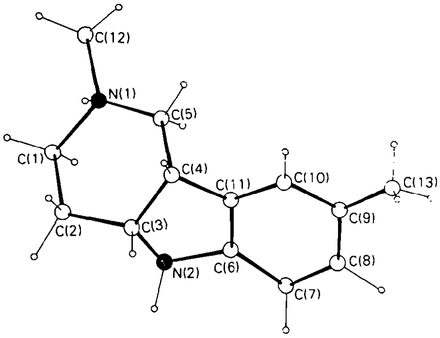

Fig. 2. View of the (–)DB1021 cation.

evidence for proton transfer comes from the carboxyl-group dimensions, C(14)–O(1) = 1·239 (3) and C(14)–O(2) = 1·249 (3) Å, and there is no doubt about the ionic nature of the carboxyl moieties. The intermolecular distances all indicate van der Waals interactions except for the distances between the protonated N(1)$^+$ and O(1) and O(2) of the deprotonated carboxyl group of *S,S*-DBTA, which are 3·077 (3) and 2·754 (2) Å respectively. An N(1)$^+$–H···O(2) hydrogen bond [H···O(2) = 1·76 (2) Å] is clearly indicated, while the second contact may be either part of a bifurcated hydrogen bond or just a van der Waals contact; because of the rather long N(1)$^+$···O(1) distance we prefer the latter possibility.

All bond lengths (Table 2) have values close to those generally expected. The mean values for N(1)$^+$–C(sp^3), C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) in the (–)DB1021 cation are 1·494, 1·525 and 1·498 Å respectively. Valence angles at the atoms involved in the ring junctions are considerably distorted from ideal values, indicating strain. The unsaturated five-membered ring is *cis*-fused with the six-membered hetero ring and adopts an envelope form with small puckering [C(3) is 0·490 (2) Å from the mean plane through the four remaining atoms] and high mirror-plane symmetry as shown by the asymmetry parameter (Duax & Norton, 1975), ΔC_s[C(3)] = 3·2°. The six-membered hetero ring adopts a distorted chair conformation with the C(12) methyl attached equatorially. The distortion involves loss of rotation symmetry, ΔC_2[C(1), C(2)] = 21·7°, with retention of the orthogonal mirror plane, ΔC_s[N(1)] = 3·0° [ring flattened at C(3)].

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Programs for the* IBM/360 *System*. Accession Nos. 133–147 in *J. Appl. Cryst.* (1973). **6**, 309–346.

Baggio, R., Woolfson, M. M., Declercq, J.-P. & Germain, G. (1978). *Acta Cryst.* A**34**, 883–892.

Duax, W. L. & Norton, D. A. (1975). In *Atlas of Steroid Structure*, Vol. 1. New York: Plenum.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1985). C**41**, 210–212

The Structure of *N*-Aminophthalimide, $\mathrm{C}_8\mathrm{H}_6\mathrm{N}_2\mathrm{O}_2$

By James H. Loehlin

Department of Chemistry, Wellesley College, Wellesley, MA 02181, *USA*

(*Received* 15 *May* 1984; *accepted* 27 *September* 1984)

Abstract. M_r = 162·15, orthorhombic, $P2_12_12_1$, a = 20·472 (14), b = 6·672 (3), c = 5·254 (3) Å, V = 717·5 (7) Å^3, Z = 4, D_m = 1·486 (8), D_x = 1·501 (2) g cm^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 1·21 cm^{-1}, F(000) = 336, T = 296 K, R = 0·046 for 779 observed reflections. With the exception of the amine hydrogens, the molecule is planar with an N–N bond length of 1·409 (3) Å. The terminal nitrogen

0108-2701/85/020210-03$01.50

atoms form a hydrogen-bonded chain along a 2_1 screw axis in the **c** direction, with a second hydrogen bond C=O···H—C connecting neighboring molecules diagonally.

Introduction. *N*-Aminophthalimide has been of interest as a novel synthon in organic syntheses (Epton, 1965; Anderson, Gilchrist, Horwell & Rees, 1970; Felix, Mueller, Horn, Joos, Schreiber & Eschenmoser, 1972). It shows significant reactivity with anhydrides but not with esters (Hearn & Prisch, 1981), with aldehydes but not with ketones and does not undergo hydrogenolytic cleavage of the N—N bond (Hearn & Lucero, 1982). The possibility that some of these reaction characteristics might be related to an unusual hydrazine linkage made the N—N bond length and the geometry of it and the adjacent C—N bonds of special interest in this study. Because this compound also had the potential of forming an N—N hydrogen-bonded chain, its structure was of interest to the author as part of a study of organic compounds with this feature.

Experimental. Density by suspension in tetrachloromethane/diethyl ether. Crystal 0·11 × 0·15 × 0·30 mm from ethanol solution, material synthesized by Professor Hearn. Syntex $P2_1$ diffractometer, graphite monochromator. Lattice parameters determined using 24 reflections with 2θ between 14 and 25°. Reflections measured to $\sin\theta/\lambda = 0{\cdot}62$ Å^{-1}. h 0–25, k −8–8, l 0–6. Lorentz and polarization corrections, absorption ignored. Three reference reflections showed no significant drift. 1665 measured reflections, 898 unique reflections, 119 with $F < 2\sigma(F)$ not used in refinement. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Benzo hydrogens in calculated positions with C—H 0·95 Å. Refinement based on F with non-hydrogens anisotropic, following isotropic refinement. Amine hydrogens located on Fourier difference map and refined isotropically. 118 variables refined giving $R = 0{\cdot}046$, $wR = 0{\cdot}050$, $S = 1{\cdot}091$. $(\Delta/\sigma)_{\max} = 0{\cdot}020$. Secondary extinction $r^* = 2{\cdot}9\,(5) \times 10^{-3}$, where $F_c^* = k|F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$ (Larson, 1970). Final difference electron density $|\rho| < 0{\cdot}25$ e Å^{-3}. $1/w = \sigma(F)^2 + (0{\cdot}030|F_o|)^2$ with $\sigma(F)$ from counting statistics. Atomic scattering factors from *International Tables for X-ray Crystallography* (1968) with anomalous-dispersion factors from Cromer & Liberman (1970). Data reduction, structure refinement and analysis were carried out using *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).†

Discussion. The molecule, with its numbering scheme, is shown in Fig. 1 and the final fractional coordinates are listed in Table 1.

The molecule is essentially planar with all deviations of non-hydrogen atoms from the least-squares plane being less than 0·014 Å. This structure implies sp^2 hybridization of the ring nitrogen atom with the lone-pair electrons available for π bonding. The hydrogen-atom positions on the terminal nitrogen indicate that, at least in the solid state, the π system does not extend to it and sp^3 hybridization fits the resulting structure well. The unusual reactivities of the hydrazide are thus probably caused by steric effects of the two acyl groups attached to the ring nitrogen atom or to the delocalization of the lone-pair electrons on it rather than to an unusually strong nitrogen–nitrogen bond.

Comparison of the N—N bond length in this structure with those in previously determined acyl hydrazides shows that it is shorter than most when compared to seven N—N bonds in five monoacyl hydrazide structures (Chieh, 1973; Jensen, 1956; Jensen & Lingafelter, 1961; Miravitlles, Briansó & Font-Altaba, 1972; Miravitlles, Briansó, Plana & Font-Altaba, 1975) with a mean length of 1·415 Å, but

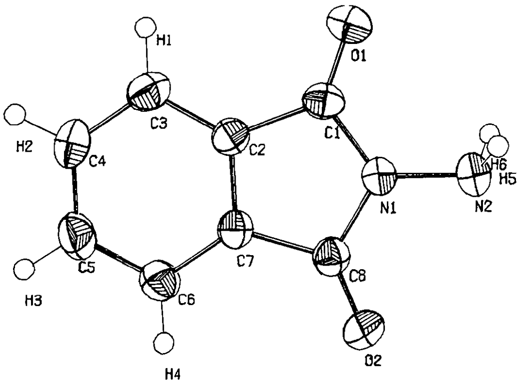

Fig. 1. *N*-Aminophthalimide viewed approximately normal to the molecular plane showing 50% probability thermal ellipsoids for the non-hydrogen atoms (*ORTEP*; Johnson, 1965).

Table 1. *Atom positions and equivalent isotropic thermal parameters*

$U_{\text{eq}} = \frac{1}{3}\sum_i U_{ii}$.

	x	y	z	U_{eq}(Å^2)
N(2)	0·2113 (1)	0·9327 (4)	0·5226 (7)	0·042 (2)
N(1)	0·1760 (1)	0·7569 (4)	0·4667 (5)	0·034 (1)
O(1)	0·0982 (1)	0·7696 (4)	0·7831 (5)	0·051 (1)
O(2)	0·2381 (1)	0·6589 (3)	0·1204 (5)	0·045 (1)
C(1)	0·1221 (1)	0·6868 (5)	0·6006 (6)	0·034 (2)
C(2)	0·1026 (1)	0·4984 (4)	0·4731 (6)	0·032 (2)
C(3)	0·0524 (1)	0·3671 (5)	0·5286 (7)	0·040 (2)
C(4)	0·0458 (2)	0·2014 (5)	0·3720 (7)	0·044 (2)
C(5)	0·0874 (2)	0·1681 (5)	0·1687 (7)	0·045 (2)
C(6)	0·1382 (2)	0·3019 (5)	0·1136 (6)	0·040 (2)
C(7)	0·1445 (1)	0·4665 (4)	0·2698 (6)	0·030 (2)
C(8)	0·1932 (1)	0·6325 (4)	0·2634 (7)	0·032 (2)
H(5)	0·225 (2)	0·928 (6)	0·696 (9)	0·034 (13)
H(6)	0·182 (2)	1·041 (6)	0·523 (8)	0·026 (11)

---

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39787 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

significantly longer than two other nitrogen-substituted phthalimides, *N*-(*N*-methylanilino)phthalimide (Barlow, Davidson, Lewis & Russell, 1979) with a 1·38 (1) Å bond and *N,N'*-biphthalimide (Apreda, Foces-Foces, Cano & García-Blanco, 1978) with a 1·372 (4) Å bond. These facts appear to be consistent with a model where localization of the lone-pair electrons on one nitrogen atom increases the bond length to the adjacent nitrogen owing to electron repulsion. The diacyl hetero-atom ring in this structure allows more delocalization than that present in the monoacyl hydrazides. In the other phthalimides, the possibility of electron delocalization from both nitrogen atoms results in significantly shorter bonds. Other bonds in this structure are similar to those in the above substituted phthalimides.

The terminal nitrogen atom of each molecule forms a hydrogen-bonded chain along a 2_1 screw axis in the **c** direction. The geometry is favorable for hydrogen bonding between H(5) and the assumed position of the lone-pair electrons on the adjacent molecule's N(2). Within the standard deviation, the molecular plane bisects the dihedral angle between the two amine protons. A second hydrogen bond appears to connect each molecule to its neighbor in the unit cell diagonally in the **b** and **c** directions, linking C(5) *via* H(3) (not refined) to O(1''). These hydrogen bonds are pictured in Fig. 2 and the distances and angles, based on the final model, are shown in Table 2.

The geometry of the hydrogen-bonded chain suggests that this substance might have significant proton conductivity in the **c** direction, closely analogous to that observed in $Li(N_2H_5)SO_4$ (Vanderkooy, Cuthbert & Petch, 1964). This possibility is currently under investigation.

I wish to express my thanks to Professor Bruce M. Foxman of Brandeis University for the use of his diffractometer: for helpful discussions related to this work to Professors Foxman, Hearn and William B. Euler of the University of Rhode Island and for assistance with early stages of the work to Alexandra P. Norton and Angela M. Schmidt. This work was supported in part by a Brachman Hoffman grant.

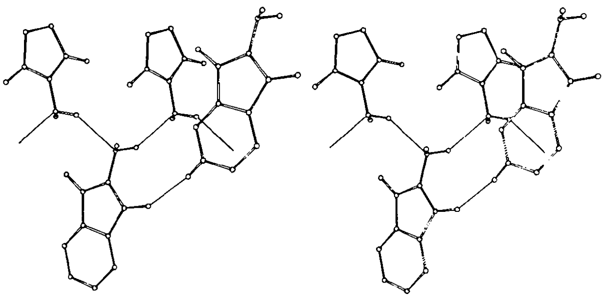

Fig. 2. An *ORTEP* stereoscopic view normal to the 2_1 screw axis in the **c** direction showing a portion of the hydrogen-bonded amine chain and the O(1'')···C(5) hydrogen bond. Hydrogens on atoms not involved in hydrogen bonding have been omitted.

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1)–N(2)	1·409 (3)	C(5)–C(6)	1·400 (4)
N(1)–C(1)	1·389 (4)	C(6)–C(7)	1·377 (4)
C(1)–O(1)	1·210 (4)	C(7)–C(8)	1·490 (4)
C(1)–C(2)	1·479 (4)	C(8)–O(2)	1·200 (4)
C(2)–C(3)	1·382 (4)	C(8)–N(1)	1·398 (4)
C(2)–C(7)	1·387 (4)	N(2)–H(5)	0·95 (4)
C(3)–C(4)	1·384 (5)	N(2)–H(6)	0·94 (3)
C(4)–C(5)	1·383 (5)		
N(2)–N(1)–C(1)	125·6 (2)	C(4)–C(5)–C(6)	120·9 (3)
N(2)–N(1)–C(8)	121·6 (2)	C(5)–C(6)–C(7)	117·1 (3)
C(1)–N(1)–C(8)	112·8 (2)	C(2)–C(7)–C(6)	121·5 (3)
N(1)–C(1)–O(1)	124·6 (3)	C(2)–C(7)–C(8)	108·5 (3)
N(1)–C(1)–C(2)	105·7 (2)	C(6)–C(7) C(8)	130·0 (3)
O(1)–C(1)–C(2)	129·6 (3)	N(1)–C(8)–O(2)	125·7 (3)
C(1)–C(2)–C(3)	130·1 (3)	N(1)–C(8)–C(7)	104·6 (2)
C(1)–C(2)–C(7)	108·2 (2)	O(2)–C(8)–C(7)	129·5 (3)
C(3)–C(2)–C(7)	121·7 (3)	N(1)–N(2)–H(5)	108 (2)
C(2)–C(3)–C(4)	116·9 (3)	N(1)–N(2)–H(6)	108 (2)
C(3)–C(4)–C(5)	121·8 (3)	H(5)–N(2)–H(6)	102 (3)
Hydrogen bonds			
N(2)···N(2')	3·197 (5)	N(2)–H(5)···N(2')	148 (3)
N(2)···H(5')	2·35 (5)	N(1)–N(2)···H(5')	118 (2)
O(1'')···C(5)	3·349 (5)	C(5)–H(3)*···O(1'')	164
O(1'')···H(3)*	2·43	H(3)*···O(1'')–C(1'')	154

* Calculated position.

References

Anderson, D., Gilchrist, T., Horwell, D. & Rees, C. W. (1970). *J. Chem. Soc.* pp. 576–582.

Apreda, M. C., Foces-Foces, C., Cano, F. H. & García-Blanco, S. (1978). *Acta Cryst.* B**34**, 3477–3479.

Barlow, J. H., Davidson, R. S., Lewis, A. & Russell, D. R. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 1103–1109.

Chieh, P. C. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 1825–1828.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **5**, 1891–1898.

Epton, R. (1965). *Chem. Ind.* (*London*), pp. 425–426.

Felix, D., Mueller, R., Horn, U., Joos, R., Schreiber, J. & Eschenmoser, A. (1972). *Helv. Chim. Acta*, **55**, 1276–1319.

Hearn, M. J. & Lucero, E. R. (1982). *J. Heterocycl. Chem.* **19**, 1537–1539.

Hearn, M. J. & Prisch, S. B. (1981). *Org. Prep. Proced. Int.* **13**, 421–424.

International Tables for X-ray Crystallography (1968). Vol. III. 2nd ed., pp. 202–205. Birmingham: Kynoch Press.

Jensen, L. H. (1956). *J. Am. Chem. Soc.* **78**, 3993–3999.

Jensen, L. H. & Lingafelter, E. C. (1961). *Acta Cryst.* **14**, 507–520.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 209–213. Copenhagen: Munksgaard.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Miravitlles, C., Briansó, J. L. & Font-Altaba, M. (1972). *Acta Geol. Hisp.* **7**, 88–93.

Miravitlles, C., Briansó, J. L., Plana, F. & Font-Altaba, M. (1975). *Acta Geol. Hisp.* **10**, 10–16.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Vanderkooy, J., Cuthbert, J. D. & Petch, H. E. (1964). *Can. J. Phys.* **42**, 1871–1878.