

- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.
- CULLICK, A. & GERKIN, R. E. (1977). *Chem. Phys.* **23**, 217–230.
- DEJACE, J. (1969). *Bull. Soc. Fr. Minéral. Cristallogr.* **92**, 141–159.
- DELUGEARD, Y., DESUCHE, J. & BAUDOUR, J. L. (1976). *Acta Cryst.* **B32**, 702–705.
- DEWAR, M. J. S., HARGET, A. J. (1970). *Proc. R. Soc. London Ser. A*, **315**, 443–455.
- ELLENSON, W. D. & KJEMS, J. K. (1977). *J. Chem. Phys.* **67**, 3619–3623.
- FRIEDMAN, P. S., KOPELMAN, R. & PRASAD, P. N. (1974). *Chem. Phys. Lett.* **24**, 15–17.
- GIRARD, A., CAILLEAU, H., MARQUETON, Y. & ECOLIVET, C. (1978). *Chem. Phys. Lett.* **54**, 479–482.
- GRÄNICHER, H. & MÜLLER, K. A. (1971). *Mater. Res. Bull.* **6**, 977–987.
- HANSON, D. M. (1975). *J. Chem. Phys.* **63**, 5046–5047.
- HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* **15**, 365–373.
- HOCHSTRASSER, R. M., MCALPINE, R. D. & WHITEMAN, J. D. (1973). *J. Chem. Phys.* **58**, 5078–5088.
- HOCHSTRASSER, R. M., SCOTT, G. W., ZEWAİL, A. M. & FUESS, H. (1975). *Chem. Phys.* **11**, 273–279.
- HÜLLER, A. & PRESS, W. (1972). *Phys. Rev. Lett.* **29**, 266–269.
- LISENSKY, G. C., JOHNSON, C. K. & LEVY, H. A. (1976). *Acta Cryst.* **B32**, 2188–2197.
- MESSAGER, J. C., SANQUER, M., BAUDOUR, J. L. & MEINNEL, J. (1973). First European Crystallographic Meeting, Bordeaux.
- PRESS, W. & HÜLLER, A. (1973). *Phys. Rev. Lett.* **30**, 1207–1211.
- PRESS, W., HÜLLER, A., STILLER, H., STIRLING, W. & CURRAT, R. (1974). *Phys. Rev. Lett.* **32**, 1354–1356.
- RIETVELD, H. M., MASLEN, E. N. & CLEWS, C. J. B. (1970). *Acta Cryst.* **B26**, 693–706.
- ROBERTSON, G. (1961). *Nature (London)*, **191**, 593–594.
- SCHMID, B. D. & BROSA, B. (1972). *J. Chem. Phys.* **56**, 6267–6268.
- SHAPIRO, S. M., AXE, J. P., SHIRANE, G. & RISTE, T. (1972). *Phys. Rev. B*, **6**, 4332–4341.
- SHNEIDER, T. & STOLL, E. (1974). *Phys. Rev. B*, **10**, 2004–2013.
- SUZUKI, H. (1959). *Bull. Chem. Soc. Jpn*, **32**, 1340–1350.
- TERAUCHI, H., SAKAI, T. & CHIHARA, H. (1975). *J. Chem. Phys.* **62**, 3832–3833.
- TROTTER, J. (1961). *Acta Cryst.* **14**, 1135–1140.
- VILLERMAIN-LECOLLIER, G., WYNCKE, B. & HADNI, A. (1971). *J. Chim. Phys. Phys. Chim. Biol.* **68**, 1606–1607.
- WYNCKE, B., BREHAT, F. & HADNI, A. (1977). *J. Phys. (Paris)*, **38**, 1171–1176.

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Nitromalonamide. A C–OH Acid with a Very Short Intramolecular O···O Hydrogen Bond

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Abstract

$C_3H_5N_3O_4$, orthorhombic, $P2_12_12_1$, $a = 4.8411$ (3), $b = 5.0206$ (2), $c = 22.582$ (2) Å, $Z = 4$, $D_m = 1.78$, $D_x = 1.78$ Mg m⁻³. The molecule has a nearly planar configuration. A part of the molecule forms a six-membered enol-like ring system including the acidic H atom, which is asymmetrically situated between the two amide O atoms. The distance between these two hydrogen-bonded O atoms is only 2.384 (4) Å.

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Introduction

This structure determination is part of a study of aliphatic nitro compounds, nitronate salts and tautomeric forms of these compounds.

Nitromalonamide is reported to have an acidity constant $K_a = 10^{-3.23}$ (Hantzsch, 1907). Therefore, there might be some doubt about the description of the molecule as a C–H acid. This structure determination was carried out especially to clarify the bonding conditions of the acid function.

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The substance was prepared from malonamide by nitration as described by Ratz (1904). Suitable single crystals were obtained from a 2-methoxyethanol solution by evaporation at room temperature. Unit-cell dimensions were determined by a least-squares refinement of data from a Guinier powder photograph taken with Cu $K\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) and calibrated with silicon as an internal standard.

A single crystal with dimensions $0.06 \times 0.15 \times 0.19$ mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromatized Mo $K\alpha$ radiation. All reflections hkl and $h\bar{k}l$ in the range $2.5 < \theta < 30^\circ$ were measured applying the ω -scan technique with $\Delta\omega = 1.00^\circ + 0.35^\circ \tan \theta$. The intensities were corrected for Lorentz and polarization effects, but no corrections for absorption or extinction were made. Symmetry-equivalent reflections were merged to produce a unique set of 970 reflections of which 533 having $F^2 > 2.5\sigma(F^2)$ were used in the structure refinement.

The structure was solved by direct methods and refined by full-matrix minimization of $\sum w(|F_o| - |F_c|)^2$ using the *SHELX 76* system of crystallographic programs (Sheldrick, 1976). Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Isotropic thermal parameters were used for H and anisotropic were used for the heavier atoms. A weighting scheme of the type: $w = 1/[\sigma^2(F_o) + c|F_o|^2]$ was applied ($c = 0.00072$ in the final cycle). At convergence [$\Delta(p) < 0.1\sigma(p)$] the residuals were: $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.037$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2} = 0.039$. Final atomic parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and reflection angles from the Guinier powder photograph have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34031 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates with standard deviations ($\times 10^4$, for H $\times 10^3$)*

	x	y	z
O(1)	3111 (5)	2182 (5)	1549 (1)
O(3)	6694 (6)	3943 (5)	2158 (1)
O(21)	4765 (6)	8023 (5)	365 (1)
O(22)	8103 (6)	9536 (5)	901 (1)
N(1)	1990 (7)	3836 (8)	671 (1)
N(2)	6193 (6)	7902 (6)	823 (1)
N(3)	9226 (7)	7531 (7)	1925 (1)
C(1)	3517 (7)	3981 (7)	1143 (1)
C(2)	5667 (7)	5931 (7)	1244 (1)
C(3)	7250 (7)	5815 (7)	1792 (1)
H(1)	449 (11)	251 (11)	188 (2)
H(11)	68 (10)	251 (10)	61 (2)
H(12)	216 (11)	497 (9)	42 (2)
H(31)	978 (7)	887 (9)	165 (2)
H(32)	1026 (11)	728 (10)	223 (2)

Discussion

The atoms C(1), C(2), C(3), N(2) lie in a plane (Table 2), and the bond angles around the C(2) atom are close to 120° (Fig. 1). All H atoms were located from a difference synthesis and none were within bonding distance of C(2). Hence the C(2) atom must be sp^2 -hybridized.

The acidic H(1) atom is situated between the two amide O atoms, and the dimensions of the hydrogen bond are O—H 1.01 (5), H...O 1.44 (5) and O...O 2.384 (4) Å. This represents one of the shortest hydrogen bonds between two O atoms reported so far. The asymmetric position of H(1) is considered significant as [O(3)—H(1)] — [O(1)—H(1)] is about six times the e.s.d. of the difference. The C atoms, the amide O atoms and the acidic H atom constitute a six-membered enol-like ring system like that found in dibenzoylmethane (Williams, 1966). The N—O distances in the nitro group are of equal length, whereas the difference between the two C—O bonds is probably significant. This is taken as further evidence of the enol-like structure and the stated position of H(1) (Fig. 1).

The crystal structures of three malonamides have been reported previously (Table 3). Comparison of nitromalonamide with these compounds reveals some differences: shortenings are seen for the bonds C(1)—C(2) and C(2)—C(3), whereas C(1)—O(1) and C(3)—O(3) are elongated. There are no significant differences concerning the C—NH₂ distances. The C(2)—N(2) bond is a little longer than is usual for nitronates (Table 3). The bonds C(2)—N(2), C(1)—O(1) and O(1)—H(1) compare well with the corresponding bonds in the related compound dilituric acid.

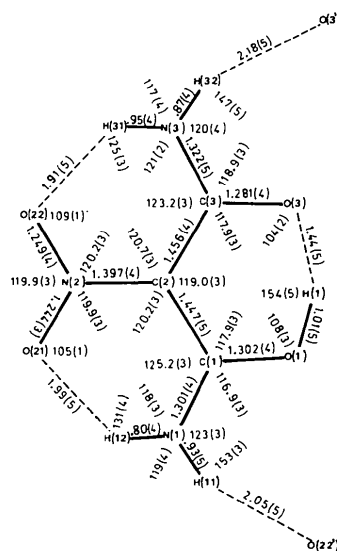


Fig. 1. Bond distances (Å), angles ($^\circ$) and the atom-numbering scheme for nitromalonamide. Estimated standard deviations are given in parentheses.

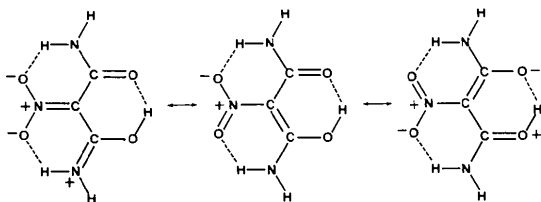
Table 2. Distances of atoms (Å) from the least-squares plane

The plane is in the form $-3.22155x + 3.01554y + 10.00843z = 1.21056$. The coordinates x , y and z are expressed parallel to the axial directions a , b and c .

N(2)*	0.001	O(3)	-0.018	H(1)	-0.021
C(1)*	0.001	O(21)	0.039	H(11)	-0.058
C(2)*	-0.003	O(22)	-0.044	H(12)	0.012
C(3)*	0.001	N(1)	-0.023	H(31)	-0.034
O(1)	-0.004	N(3)	0.015	H(32)	-0.082

* These atoms define the least-squares plane.

From the information contained in Table 3 we conclude that there must be an appreciable degree of delocalization over all the non-hydrogen atoms. This is supported by the planarity of the molecule (Table 2). Thus the molecular structure cannot be expressed in a satisfactory way by a single canonical formula. Among the many possible mesomeric structures, we have chosen the following three to show the delocalizing ability of the molecule.



Three of the H atoms form intramolecular hydrogen bonds to the nitro-oxygen and the amide-oxygen atoms (Fig. 2), the other two H atoms join the molecules to form dimolecular layers. The intermolecular hydrogen bonds make up two types of spirals, *P* and *Q*, centered

on the 2_1 axes parallel to b (Fig. 2). Molecules I, IV and V represent one turn of the spiral *P*. II, III, IV and V represent one turn of the other spiral, *Q*.

We wish to express our appreciation to Dr L. D. Barron for his careful study of the manuscript.

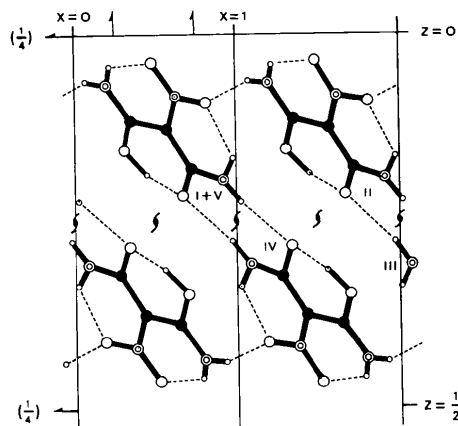


Fig. 2. View of the packing of the crystal structure (b -axis projection). The dotted lines represent the hydrogen-bonding system.

References

- BOLTON, W. (1963). *Acta Cryst.* **16**, 950–956.
 CHIEH, P. C., SUBRAMANIAN, E. & TROTTER, J. (1970). *J. Chem. Soc. A*, pp. 179–184.
 HANTZSCH, A. (1907). *Chem. Ber.* **40**, 1523–1532.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
 KLEWE, B. (1972). *Acta Chem. Scand.* **26**, 1049–1057.

Table 3. Bond lengths (Å) in nitromalonamide compared with corresponding bonds in related compounds

NITRMA: nitromalonamide. USUBMA: malonamide (Chieh, Subramanian & Trotter, 1970). BROMMA: bromomalonamide (Picone & Rogers, 1974). DICLMA: dichloromalonamide (Lerbscher, Krishna Rao & Trotter, 1971). TETRNI: dirubidium 1,1,2,2-tetranitroethanediide (Klewe, 1972). DIPONI: dipotassium nitroacetate (Sutor, Llewellyn & Maslen, 1954). NITRBA: 5-nitrobarbituric acid = diluturic acid (Bolton, 1963). DIBZME: dibenzoylmethane (Williams, 1966).

	C—C	C—O	C—NH ₂	C—NO ₂	N—O	C—OH	CO—H	OH...O	H—N	NH...O
NITRMA	1.456 1.447	1.281	1.322 1.301	1.397	1.249 1.244	1.302	1.01	1.44	0.80 0.95	2.18 2.05
USUBMA	1.503– 1.513	1.240– 1.242	1.309– 1.321						0.82– 1.02	1.94– 2.20
BROMMA	1.522	1.236	1.290						0.92 1.11	1.85 2.21
DICLMA	1.560	1.219	1.320						0.91 0.91	2.21 2.06
TETRNI				1.378 1.381	1.234– 1.251					
DIPONI				1.39 1.28	1.26 1.22					
NITRBA	1.408 1.452			1.406	1.222 1.259	1.302	0.99	1.56		
DIBZME		1.292				1.317	1.18	1.34		

- LERBSCHER, J. A., KRISHNA RAO, K. V. & TROTTER, J. (1971). *J. Chem. Soc. A*, pp. 1505–1508.
- PICONE, R. F. & ROGERS, M. T. (1974). *J. Chem. Phys.* **61**, 4808–4813.
- RATZ, F. (1904). *Monatsh. Chem.* **25**, 55–123.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SUTOR, D. J., LLEWELLYN, F. J. & MASLEN, H. S. (1954). *Acta Cryst.* **7**, 145–152.
- WILLIAMS, D. E. (1966). *Acta Cryst.* **21**, 340–348.

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The Crystal Structure of *o*-(Bromomethyl)benzonitrile

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Abstract

o-(Bromomethyl)benzonitrile, C_8H_6BrN , is monoclinic with unit-cell dimensions $a = 12.69$ (3), $b = 8.16$ (4), $c = 7.24$ (2) Å and $\beta = 98.2$ (2)°. The space group is $P2_1/a$ and the calculated density with four formula units in the unit cell is 1.740 Mg m^{-3} . Intensities were collected on a Weissenberg camera using Cu $K\alpha$ radiation. The intensities of the reflections were visually estimated. The structure was determined by the heavy-atom technique and refined by the full-matrix least-squares method to $R = 0.095$ for 519 observed reflections. No angle in the benzyl ring differs significantly from the mean of 119.9° , nor C–C bond length from the mean of 1.41 Å; the lengths of C(1)–C(2) and C(7)–C(8) do not differ significantly.

Introduction

o-(Bromomethyl)benzonitrile, C_8H_6BrN , is important as a chemical reagent in the synthesis of heterocyclic compounds (Fuson, 1926). An X-ray investigation was undertaken to ascertain the stereochemistry of the molecule and the structure of the compound in the crystalline state.

Experimental

The crystals of the title compound used for this work were prepared by the method described by Fuson (1926). Single crystals were selected for X-ray diffraction work and being hygroscopic were sealed in Lindemann-glass capillaries of very low absorption.

The unit-cell dimensions were obtained from Weissenberg photographs using Ag lines superimposed as an internal standard. Preliminary optical and X-ray

examination of the crystals indicated that they are monoclinic. The space group was found to be $P2_1/a$ on the basis of systematic absences of reflections observed ($h0l$: $h = 2n + 1$; $0k0$: $k = 2n + 1$).

The unit-cell dimensions at room temperature ($\approx 303 \text{ K}$) are: $a = 12.69$ (3), $b = 8.16$ (4), $c = 7.24$ (2) Å and $\beta = 98.2$ (2)°. The density, 1.708 (5) Mg m^{-3} , measured by flotation in zinc chloride solution agrees with the value, 1.740 Mg m^{-3} , calculated for four formula units with $M_r = 195.9$ in the cell of volume 743.02 Å^3 . Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation by use of the multiple-film method. Intensities were measured by visual comparison with a calibrated intensity scale. The data were corrected for Lorentz, polarization and spot-extension effects (Phillips, 1954, 1956). The absorption correction was neglected but a type I extinction correction (Zachariasen, 1967) was applied in the last stages of refinement. The value of the extinction constant γ is 0.44 (6).

Structure determination and refinement

The structure was solved by identifying the Br–Br vectors in a three-dimensional Patterson synthesis. A three-dimensional Fourier synthesis based only on phases due to the Br-atom contribution revealed the positions of all the non-hydrogen atoms. The proposed structure was stereochemically satisfactory. The R factor at this stage was 0.21 .

The structure was then refined by the full-matrix least-squares method. The program used was the modified version of the *ORFLS* program of Busing, Martin & Levy (1962). The function minimized in the least-squares calculation was $\sum w(F_o - F_c)^2$, where the summation was over all reflections and w was the weighting factor. A plot of $w(\Delta F)^2$ as a function of