

- SHELDRIK, G. M. (1980). *SHELXS80* – enlarged version of *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England, and Göttingen, Germany.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Germany.
- VINOGRADOVA, L. F., GAIWORONSKAYA, L. A., KIRILLOVA, L. M., BU HABIB, H. & PROSTAKOV, N. S. (1984). *Khim. Farm. Zh.* **18**, 170–173.
- WATERMAN, P. G. & MUHAMMAD, I. (1985). *Phytochemistry*, **24**, 523–527.
- WIECZOREK, J. S., BODUSZEK, B., GANCARZ, R. & ZUKIEWICZ, G. (1984). Polish patent PL 123, 716(CI.C07F9/38), 31 Jan 1984. [Appl. 223, 761, 24 Apr. 1980. 2pp.]
- WU, J. C. (1989). *Heterocycles*, **29**, 463–475.
- ZANKOWSKA-JASIŃSKA, W. & KOLASA, A. (1976). *Ann. Soc. Chim. Polonorum*, **50**, 625–645.

Acta Cryst. (1992). **C48**, 1260–1262

Structure of 4-Bromopyrazabole

BY THOMAS G. HODGKINS

Department of Chemistry, University of Wisconsin, Whitewater, Wisconsin 53190, USA

AND DOUGLAS R. POWELL

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

(Received 13 September 1991; accepted 21 November 1991)

Abstract. C₆H₉B₂BrN₄, $M_r = 238.7$, monoclinic, $P2_1/n$, $a = 6.756$ (2), $b = 13.012$ (4), $c = 10.931$ (4) Å, $\beta = 91.50$ (2)°, $V = 960.6$ (5) Å³, $Z = 4$, $D_x = 1.650$ Mg m⁻³, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 5.510$ mm⁻¹, $F(000) = 472$, $T = 108$ (2) K, $R = 4.45\%$, 1185 unique observed data. The molecule has a butterfly arrangement of three condensed rings with a boat-shaped central B₂N₄ moiety. The Br is bonded to the B in an axial position with a B—Br length of 2.075 (5) Å. The shorter B—N bond distances in the N₂BHBr group [1.530 (6) Å ave.] compared to the B—N bonds in the N₂BH₂ group [1.562 (7) Å ave.] suggest that the N₂BHBr group is the stronger Lewis acid.

Introduction. The synthesis of pyrazabole and a few of its derivatives was first reported by Trofimenko (1966). Since then, dozens of other pyrazaboles have been reported; this subject was recently reviewed by Niedenzu (1988). The compound 4-bromopyrazabole was found to be thermally unstable with respect to formation of 4,8-dibromopyrazabole and pyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1985). A study of the crystal structure of 4-bromopyrazabole was undertaken to look for structural reasons for this instability.

Experimental. A sample of 4-bromopyrazabole was synthesized from boron tribromide and a molar excess of pyrazabole according to Hanecker, Hodgkins, Niedenzu & Nöth (1985). Unreacted pyrazabole was removed by sublimation over a three day

period at bath temperatures of 312–316 K. A small portion of the white powdery residue was then placed in an ampoule, and the ampoule was sealed under vacuum. The bottom 1 cm of this ampoule was heated in a mineral bath at bath temperatures of 313–318 K; the rest of the ampoule was cooled to ambient temperature by a stream of air. During the next 22 d, colorless prismatic crystals were slowly deposited on the inside surface of the ampoule just above the level of the mineral oil.

A colorless prism of dimensions 0.20 × 0.25 × 0.45 mm was mounted on a Syntex *P1* diffractometer equipped with a nitrogen gas-stream sample cooler. Cell parameters were determined from the setting angles of 24 intensity maxima with 2θ values from 41 to 50°. Intensity data were measured using ω scans with a scan range of 0.40° and a variable scan speed of 2 to 12° min⁻¹. Stationary crystal/stationary counter background measurements were made 0.8° ω above and below peak maxima for 16.7% of the total scan time. A semi-empirical absorption correction was applied to the data giving minimum and maximum transmission factors of 0.007 and 0.743. Intensity data were collected in the 2θ range 3.5 to 114° with $-7 \leq h \leq 2$, $0 \leq k \leq 14$, $-11 \leq l \leq 11$. Three standard peaks ($\bar{3}1\bar{3}$, $2\bar{5}1$, 035) were remeasured every 50 data with a maximum variation of 0.02. The 1949 measured data were merged giving 1293 unique data with $R_{int} = 6.49\%$. The structure was solved by direct methods. The structure was refined by full-matrix least squares on F using 1185 observed [$F > 4\sigma(F)$] data. Initial positions of H

Table 1. Atomic coordinates and isotropic equivalent thermal parameters ($\text{\AA}^2 \times 10^4$)

	x	y	z	U_{eq}^*
C(1)	-0.1395 (7)	0.1011 (4)	0.6371 (5)	299 (15)
C(2)	0.0398 (8)	0.1185 (3)	0.5821 (6)	343 (17)
C(3)	0.1589 (6)	0.1630 (3)	0.6719 (4)	323 (15)
N(3a)	0.0561 (4)	0.1735 (3)	0.7736 (3)	232 (11)
B(4)	0.1126 (7)	0.2274 (4)	0.8939 (5)	261 (15)
N(4a)	0.0096 (5)	0.1689 (3)	0.9956 (3)	257 (11)
C(5)	0.0714 (8)	0.1476 (4)	1.1114 (5)	354 (16)
C(6)	-0.0692 (8)	0.0930 (4)	1.1678 (5)	407 (18)
C(7)	-0.2204 (7)	0.0804 (3)	1.0805 (4)	357 (16)
N(7a)	-0.1714 (5)	0.1261 (2)	0.9768 (4)	253 (12)
B(8)	-0.2885 (7)	0.1390 (4)	0.8519 (6)	326 (18)
N(8a)	-0.1283 (5)	0.1349 (2)	0.7525 (4)	247 (12)
Br(1)	0.00165 (6)	0.37598 (3)	0.88390 (4)	313 (3)
H(4)	0.256 (6)	0.235 (3)	0.898 (4)	32 (4)
H(8a)	-0.399 (6)	0.074 (4)	0.854 (4)	32 (4)
H(8b)	-0.363 (6)	0.207 (3)	0.863 (4)	32 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

B(4)—Br(1)	2.075 (5)	N(4a)—C(5)	1.351 (6)
N(8a)—C(1)	1.336 (6)	N(4a)—N(7a)	1.354 (5)
C(1)—C(2)	1.385 (7)	C(5)—C(6)	1.349 (7)
C(2)—C(3)	1.380 (7)	C(6)—C(7)	1.389 (7)
C(3)—N(3a)	1.333 (6)	C(7)—N(7a)	1.330 (6)
N(3a)—B(4)	1.530 (6)	N(7a)—B(8)	1.569 (7)
N(3a)—N(8a)	1.357 (4)	B(8)—N(8a)	1.555 (7)
B(4)—N(4a)	1.530 (6)	B(8)—H(8a)	1.13 (5)
B(4)—H(4)	0.97 (4)	B(8)—H(8b)	1.03 (5)
Br(1)—B(4)—N(3a)	107.5 (3)	C(5)—N(4a)—N(7a)	108.2 (4)
Br(1)—B(4)—N(4a)	109.4 (3)	N(4a)—C(5)—C(6)	109.4 (4)
N(8a)—C(1)—C(2)	109.1 (4)	C(5)—C(6)—C(7)	105.2 (5)
C(1)—C(2)—C(3)	105.1 (5)	C(6)—C(7)—N(7a)	109.8 (4)
C(2)—C(3)—N(3a)	109.2 (4)	C(7)—N(7a)—B(8)	131.2 (4)
C(3)—N(3a)—B(4)	129.8 (3)	C(7)—N(7a)—N(4a)	107.4 (4)
C(3)—N(3a)—N(8a)	108.5 (3)	B(8)—N(7a)—N(4a)	121.4 (4)
B(4)—N(3a)—N(8a)	121.5 (3)	N(7a)—B(8)—N(8a)	105.1 (3)
N(3a)—B(4)—N(4a)	106.7 (3)	B(8)—N(8a)—C(1)	130.4 (4)
B(4)—N(4a)—C(5)	130.4 (4)	B(8)—N(8a)—N(3a)	121.5 (4)
B(4)—N(4a)—N(7a)	121.4 (3)	C(1)—N(8a)—N(3a)	108.1 (4)

atoms were calculated. Boron H positions were refined independently; positions of H atoms in the pyrazolyl ($\text{N}_2\text{C}_3\text{H}_3$) groups were refined using a riding model. Non-H atoms were refined anisotropically. A single isotropic temperature factor was refined for all H atoms. A total of 128 parameters were refined. The structure converged to $R = 4.45\%$, $wR = 5.81\%$, $S = 1.60$ with a maximum Δ/σ of 0.005. Weights used in refinement were given by $[\sigma^2(F) + 0.0008F^2]^{-1}$ with $\sigma^2(F)$ determined by counting statistics. The maximum and minimum peaks in a final difference electron density map were 1.04 and -0.73 e \AA^{-3} , respectively. The two large ($> 0.6 \text{ e \AA}^{-3}$) peaks in the difference map were located about 1.1 \AA from the Br atom. Complex, neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All programs used were from the *SHELXTL-Plus* software package (Sheldrick, 1990).

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Selected bond lengths and angles are presented in Table 2.* 4-Bromopyrazabole has a boat-shaped central B_2N_4 ring. The numbering scheme is shown in Fig. 1 and the packing in Fig. 2.

Discussion. The acute dihedral angles between the plane of the four N atoms and the two BN_2 are $30.3 (5)$ and $29.7 (3)^\circ$. These values suggest a slightly flatter boat than was seen in pyrazabole [$35.5 (1)$ and $33.4 (3)^\circ$] (Hanecker, Hodgkins, Niedenzu & Nöth, 1985). The compound 4,4,8,8-tetrabromopyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1985) sits on a crystallographic $2/m$ site and thus the B_2N_4 ring is planar.

The Br in 4-bromopyrazabole occupies an axial position on the B(4) boron atom. The B—Br length in 4-bromopyrazabole, 2.075 (5) \AA , is longer than the 2.009 (8) \AA seen in the tetrabromo compound, longer than the 2.051 \AA B—Br bond length average seen in 4,8-dibromo-2,6-dichloropyrazabole (Niedenzu & Nöth, 1983) and about the same as the 2.072 (14) \AA

* Lists of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54882 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0390]

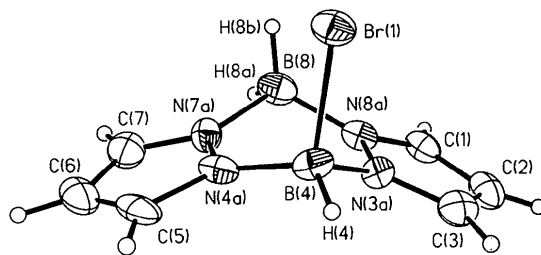


Fig. 1. Numbering scheme of 4-bromopyrazabole showing 50% probability thermal ellipsoids.

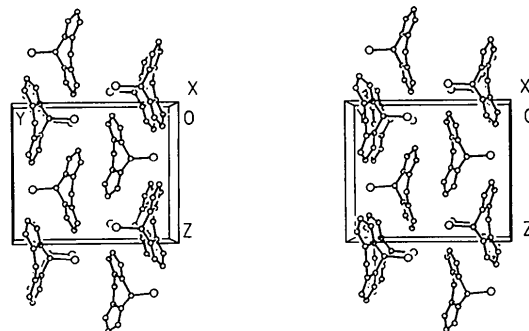


Fig. 2. Packing diagram of 4-bromopyrazabole.

seen in a dibromoboryl-phenanthroline compound (Klebe & Tranqui, 1984). This lengthening may help to explain the thermal instability of 4-bromopyrazabole relative to the two symmetrical compounds pyrazabole and 4,8-dibromopyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1985). Also, the two kinds of B—N bonds in 4-bromopyrazabole are of distinctly different lengths: N₂BHBr 1.530 (6) Å average; N₂BH₂ 1.562 (7) Å average. The latter B—N bonds are similar to those observed in pyrazabole, 1.553 (3) Å. The B—N bonds in the tetrabromo compound are 1.521 (12) Å. Thus the B atoms in these three compounds should be ranked in order of increasing Lewis acidity as: N₂BH₂, N₂BHBr, N₂BBr₂. Similar reasoning has been invoked to explain trends in B—N bond lengths in other B-halopyrazaboles (Clarke, Das, Hanecker, Mariategui, Niedenzu, Niedenzu, Nöth & Warner, 1987; Hanecker, Hodgkins, Niedenzu & Nöth, 1985).

This work was supported in part by a University of Wisconsin State Research Grant. Assistance provided by the Department of Chemistry at the University of Wisconsin-Whitewater is hereby gratefully acknowledged. Funds to purchase the X-ray diffraction equipment were provided in part by the National Science Foundation.

References

- CLARKE, C. M., DAS, M. K., HANECKER, E., MARIATEGUI, J. F., NIEDENZU, K., NIENDENZU, P. M., NÖTH, H. & WARNER, K. R. (1987). *Inorg. Chem.* **26**, 2310–2317.
 HANECKER, E., HODGKINS, T. G., NIEDENZU, K. & NÖTH, H. (1985). *Inorg. Chem.* **24**, 459–462.
 KLEBE, G. & TRANQUI, D. (1984). *Inorg. Chim. Acta*, **81**, 1–5.
 NIEDENZU, K. (1988). *Adv. Boron Boranes*, **5**, 357–372.
 NIEDENZU, K. & NÖTH, H. (1983). *Chem. Ber.* **116**, 1132–1153.
 SHELDRICK, G. M. (1990). *SHELXTL-Plus*, version 4.1. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
 TROFIMENKO, S. (1966). *J. Am. Chem. Soc.* **88**, 1842–1844.

Acta Cryst. (1992). **C48**, 1262–1265

Structure of 1-Morpholinoanthraquinone at 110 K*

BY MICHAEL KAUFMANN, DANIEL BERGER, RALPH HÄRTER AND DANIEL HIRSCHI

Institut für organische Chemie, Universität Bern, Freiestr. 3, 3012 Bern, Switzerland

AND HANS-BEAT BÜRGI, ANDREA RASELLI AND CAROLINE RÖHR

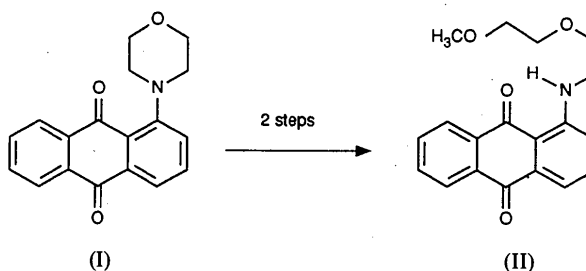
Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestr. 3, 3012 Bern, Switzerland

(Received 19 August 1991; accepted 3 December 1991)

Abstract. C₁₈H₁₅NO₃, *M_r* = 293.3, monoclinic, *P*2₁/*a*, *a* = 12.456 (2), *b* = 6.735 (4), *c* = 16.135 (3) Å, β = 92.17 (1)°, *V* = 1353 Å³, *Z* = 4, *D_x*(110 K) = 1.440, *D_x*(295 K) = 1.387, *D_m*(295 K) = 1.380 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.90 cm⁻¹, *T* = 110 K, *F*(000) = 616, final *R* = 0.034, 1889 unique reflections. A repulsive interaction between the morpholine moiety and the carbonyl oxygen (O9) is observed, which distorts the angles O9—C9—C9a [123.3 (1)°] and N1—C1—C9a [122.0 (1)°]. Both O9 and to a lesser extent O10 are bent out of the anthraquinone plane, but in opposite directions.

Introduction. The title compound 1-morpholinoanthraquinone (I) was synthesized as a precursor to

the anthraquinone-based podand (II) which is related to previously synthesized anthraquinone-based lariat ethers (Gustowski, Delgado, Gatto, Echegoyen & Gokel, 1986*a,b*; Echegoyen, Yoo, Gatto, Gokel & Echegoyen, 1989). In the course of those investigations we found that (I) is about four orders of magnitude more basic than (II) (Kaufmann, 1991).



* This structure was solved in an introductory class to X-ray crystallography.