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# A Neutron Diffraction Refinement of Lithium Hydrazinium Fluoroberyllate

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**Abstract.** $LiN_2H_5BeF_4$, orthorhombic, $Pna2_1$, $a=9{\cdot}811$ (4), $b=8{\cdot}880$ (8), $c=5{\cdot}139$ (4) Å, $Z=4$. The present neutron diffraction refinement agrees with the structure determined by X-ray diffraction although as expected the N–H bonds are systematically 0·1 Å longer in the present refinement.

**Introduction.** A single crystal with dimensions $2{\cdot}5\times2{\cdot}5\times9{\cdot}0$ mm, grown from aqueous solution (Tedenac, Vilminot, Cot, Norbert & Maurin, 1972), was used for the neutron diffraction measurements. To avoid possible decomposition caused by the high humidity around the McMaster swimming pool reactor, the crystal was coated with perfluorokerosine. The diffraction measurements were made with the McMaster neutron diffractometer (Anderson, 1973). The neutron beam, monochromated by reflexion from the (111) plane of a single copper crystal, had a wavelength of 1·091 Å. The intensities of 470 independent reflexions with $\sin\theta/\lambda<0{\cdot}65$ were measured using the $\omega$ step scanning technique. The number of steps in the scan varied from 27 for reflexions whose $2\theta$ value was $<20°$, to 45 steps for those reflexions in the range $80°\le2\theta<100°$, each step being $\frac{1}{18}°$. The first $\frac{1}{9}$ and last $\frac{1}{9}$ of the steps in each scan were used to determine the background. The duration of each step was controlled by a fission counter which monitored the main beam. A monitor count of $10^4$ for each step was used, and the approximate time for a step was one minute at a reactor power of 5 MW. The measured intensities were corrected for Lorentz effects using the locally written Fortran program *DIFDAT*. Since the absorption coefficient, including the contribution of incoherent scattering of the H atoms, is 0·21 $mm^{-1}$ (*cf.* Koetzle, Hamilton & Parthasarathy, 1972) no correction for absorption was made.

The lattice parameters were taken from the X-ray refinement (Anderson, Brown & Vilminot, 1973) from which were also obtained the values of the atomic coordinates used in the initial refinement of the structure with the neutron measurements. The coherent neutron scattering lengths reported by Bacon (1972) were used (Li: −0·214, N: 0·94, H: −0·374, Be: 0·774, F: $0{\cdot}56\times10^{-12}$ cm). Refinement of the atomic positions and isotropic temperature factors of all atoms, using the full-matrix least-squares program *CRYLSQ* of the X-RAY 71 program library system (Stewart, Kruger, Kundell & Baldwin, 1971), gave a residual index, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0·122. Further refinement with anisotropic temperature factors reduced the residual index, although the temperature factor for the lithium atom refined to a non-positive definite value and had

Table 1. *Position and temperature parameters for* $LiN_2H_5BeF_4$

Expressions used for the temperature factors are:

$\exp\,[-2\pi^2\times10^{-3}\,(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$ and $\exp\,[-2\pi^2\times10^{-3}\,U(2\sin\theta/\lambda)^2]$.

The temperature factor of Li could only be refined isotropically. Figures in parentheses are the standard errors in the last decimal places quoted.

| | $x$ | $y$ | $z$ | $U$ or $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Li | 0·3213 (18) | 0·4353 (20) | 0·2766 (86) | 33 (5) | | | | | |
| N(1) | 0·0228 (6) | 0·4107 (7) | 0·7455* | 31 (3) | 36 (3) | 61 (9) | −7 (2) | 2 (6) | 0 (5) |
| N(2) | 0·4418 (6) | 0·2219 (6) | 0·7397 (39) | 26 (3) | 31 (3) | 48 (6) | 2 (2) | 2 (6) | −6 (6) |
| Be | 0·1585 (4) | 0·1260 (5) | 0·2468 (36) | 15 (2) | 23 (2) | 31 (5) | −1 (2) | −1 (5) | 9 (5) |
| F(1) | 0·1963 (8) | 0·1058 (9) | 0·5505 (37) | 31 (4) | 25 (4) | 49 (9) | −5 (3) | −7 (5) | 10 (5) |
| F(2) | 0·0001 (6) | 0·1416 (8) | 0·2305 (41) | 14 (3) | 38 (3) | 36 (6) | −4 (2) | 4 (6) | −12 (7) |
| F(3) | 0·2263 (7) | 0·2704 (7) | 0·1447 (30) | 28 (3) | 26 (4) | 32 (9) | −8 (3) | −2 (4) | 5 (4) |
| F(4) | 0·2985 (8) | 0·4877 (8) | 0·5980 (37) | 30 (4) | 28 (4) | 53 (8) | −7 (3) | −3 (5) | −17 (5) |
| H(1) | 0·116 (1) | 0·384 (2) | 0·791 (7) | 33 (7) | 84 (10) | 86 (25) | −15 (8) | −13 (16) | −13 (17) |
| H(2) | 0·019 (2) | 0·451 (3) | 0·572 (7) | 88 (16) | 69 (15) | 28 (21) | −28 (12) | 12 (16) | 1 (12) |
| H(3) | 0·347 (1) | 0·195 (2) | 0·710 (9) | 30 (7) | 84 (11) | 145 (29) | 10 (8) | −25 (15) | 14 (19) |
| H(4) | 0·445 (3) | 0·275 (3) | 0·926 (8) | 89 (20) | 68 (13) | 83 (29) | 48 (14) | 11 (18) | −15 (15) |
| H(5) | 0·472 (2) | 0·292 (4) | 0·613 (6) | 50 (10) | 111 (17) | 14 (14) | 7 (12) | 13 (10) | 24 (13) |

* Used to define origin of space group.

to be refined isotropically. Several of the strong reflexions showed evidence of extinction effects, and an isotropic extinction correction was included in the refinement. The corrected values of $F_c$ were given by:

$$F_c^* = F_c[1 + 0{\cdot}46 \times 10^{-2} \times \beta_N(2\theta) F_c^2]^{-1/2}.$$

where $\beta_N$ is the function given by Larson (1967).

The final stages of the least-squares refinement used the local program *CUDLS*. The temperature factor of the lithium atom still could not be refined anisotropically. A refinement of the scattering length of lithium changed its value from $-0{\cdot}214 \times 10^{-12}$ to $-0{\cdot}195 \times 10^{-12}$ cm, indicating there could be a higher percentage of $^6$Li (scattering length $0{\cdot}18 \times 10^{-12}$ cm) in this sample than the 7·42% $^6$Li in naturally occurring lithium. Even so, this did not enable an anisotropic temperature factor to be used for this atom, and in the subsequent stages of the refinement the scattering length was reset to its original value of $-0{\cdot}214 \times 10^{-12}$ cm, and an isotropic temperature factor was used. During the final cycles of least-squares refinement the reflexions were weighted by $w = 1/\sigma^2$ where $\sigma$ is the standard deviation of $F_o$ estimated from the counting statistics of the measurements. The final weighted residual index, $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum F_o^2\}^{1/2}$, was 0·044, and the final atomic parameters and temperature factors are given in Table 1. The observed and calculated neutron structure factors are given by Anderson (1973).*

Table 2. *Bond distances* (Å) *and angles* (°) *involving* H *atoms*

N(1)–N(2) 1·421 (8)

Angles at N(1) subtended by

| | H(1) | H(2) | H(2′) |
|---|---|---|---|
| N(2) | 108 (1) | 105 (2) | 112 (1) |
| H(1) | | 110 (3) | 97 (2) |
| H(2) | | | 120 (2) |

Angles at N(2) subtended by

| | H(3) | H(4) | H(5) |
|---|---|---|---|
| N(1) | 109 (1) | 109 (2) | 112 (2) |
| H(3) | | 106 (3) | 110 (3) |
| H(4) | | | 108 (3) |

Dihedral angles between planes containing the N(1)–N(2) bond and

| | | |
|---|---|---|
| H(1) | H(1) | 119 |
| H(1) | H(2′) | −108 |
| H(1) | H(3) | 186 |
| H(3) | H(4) | 116 |
| H(3) | H(5) | −124 |

Table 2 (*cont.*)

Hydrogen-bond distances

| N–H···*A* | | N–H | H···*A* | N···*A* | ∠*N*–H···*A* |
|---|---|---|---|---|---|
| N(1)–H(1)··· | F(3) | 0·97 (2) | 2·34 (4) | 3·122 (13) | 137 (2) |
| | F(4) | | 2·25 (2) | 2·892 (11) | 123 (2) |
| N(1)–H(2)··· | N(1′) | 0·96 (3) | 2·12 (3) | 3·052 (5) | 163 (2) |
| N(2)–H(3)··· | F(1) | 0·97 (2) | 1·87 (3) | 2·794 (13) | 158 (3) |
| N(2)–H(4)··· | F(2) | 1·07 (4) | 1·81 (4) | 2·856 (26) | 165 (3) |
| | F(3) | | 2·42 (3) | 2·996 (19) | 112 (2) |
| N(2)–H(5)··· | F(2) | 0·95 (3) | 2·07 (4) | 2·939 (26) | 152 (3) |
| | F(1) | | 2·41 (3) | 3·086 (12) | 128 (2) |
| | F(4) | | 2·43 (3) | 2·842 (12) | 106 (2) |

**Discussion.** The present work was undertaken as part of a program to provide a clearer picture of the hydrogen bonding in hydrazinium compounds. The positional coordinates of the non-hydrogen atoms determined in the present work do not differ significantly from those found in the X-ray refinement (Anderson, Brown & Vilminot, 1973) but the hydrogen atoms are about 0·1 Å further from the nitrogen atoms. The bond lengths and angles associated with the hydrazinium group are listed in Table 2. An additional weak hydrogen bond [N(2)–H(4)···F(3)] is included here for the first time.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30882 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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