### References

Alléaume, M., Gulko, A., Herbstein, F. H., Kapon, M. & Marsh, R. E. (1976). *Acta Cryst.* B**32**, 669–682.

Biagini, S., Cannas, M. & Marongiu, G. (1969). *Acta Cryst.* B**25**, 730–737.

Chatterjee, C., Dattagupta, J. K. & Saha, N. N. (1981). *Acta Cryst.* B**37**, 1835–1838.

Chatterjee, C., Dattagupta, J. K. & Saha, N. N. (1982). *Acta Cryst.* B**38**, 1845–1847.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cruickshank, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Haridas, M., Tiwari, R. K. & Singh, T. P. (1982). *Curr. Sci.* **51**, 1111–1112.

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

Patel, U., Haridas, M. & Singh, T. P. (1983). *Z. Kristallogr.* Submitted.

Sass, R. L. (1960). *Acta Cryst.* **13**, 320–324.

Shiono, R. (1968–1971). *SFLS*. Tech. Rep. 48 and 49. Crystallography Laboratory, Univ. of Pittsburgh, PA, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175 3187.

Tiwari, R. K. (1983) Ph D Thesis, Sardar Patel Univ., Vallabh Vidyanagar.

Wilson, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

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# Radioprotectant Bis(2-guanidinoethyl) Disulfide Dihydrobromide, $C_6H_{18}N_6S_2^{2+}.2Br^-$

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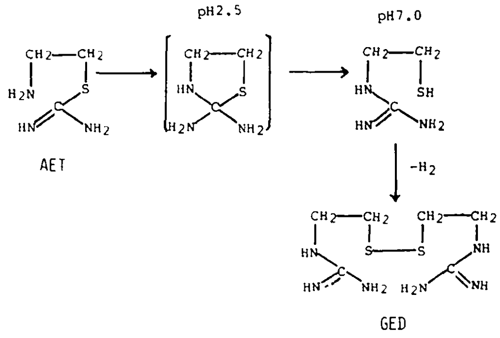
**Abstract.** $M_r = 398{\cdot}18$, orthorhombic, $Pca2_1$, $a = 24{\cdot}159\,(4)$, $b = 4{\cdot}904\,(2)$, $c = 12{\cdot}451\,(3)$ Å, $V = 1475{\cdot}0\,(7)$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}791\,(6)$, $D_x = 1{\cdot}793$ Mg m$^{-3}$, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo }K\alpha) = 6{\cdot}076$ mm$^{-1}$, $F(000) = 800$, $T = 293$ K, final $R = 0{\cdot}087$ for 861 independent reflections with $F_o \geq 3\sigma(F_o)$. The molecule takes an extended conformation with no indication of an intramolecular N···S interaction. The crystal structure is stabilized by the formation of intermolecular NH···Br and NH···S hydrogen bonds and by many short contacts.

**Introduction.** S-containing compounds such as cysteine, cysteamine and 2-(2-aminoethyl)thiouronium (AET) are well known as prominent radioprotective agents (Patt, Tyree, Straube & Smith, 1949; Herve & Bacq, 1952; Langendorff, Koch & Hagen, 1954; Doherty & Burnett, 1955; Crough & Overman, 1957; Doherty, Burnett & Shapira, 1957).

Bis(2-guanidinoethyl) disulfide (GED) synthesized by the transguanylation of AET has been shown to be a radioprotectant to an extent similar to that of AET (Hino, Tanaami, Yamada & Akaboshi, 1966*a*,*b*).



Several theories on chemical radioprotection have been proposed (for example, Hanaki & Akaboshi, 1966). Among them, the interaction of the radioprotectants with biological macromolecules such as nucleic acids is of particular importance. Thus, the elucidation of the detailed molecular geometry of these compounds is relevant to the development of these theories. As part of the structural studies on radioprotectants (Inoue, Sakaki, Wakahara & Tomita, 1978; Ishida, Shimizu, Inoue, Kitamura, Wakahara, Tomita & Shinoda, 1981), the X-ray analysis of GED dihydrobromide has been carried out.

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2).$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| Br(1) | 0·4363 (2) | −0·0423 (8) | 0·5993* | 4·1 |
| Br(2) | 0·3154 (2) | 0·0609 (8) | 0·8738 (4) | 3·7 |
| S(1) | 0·3712 (5) | 0·789 (2) | 0·171 (1) | 4·1 |
| S(1′) | 0·4126 (4) | 0·668 (2) | 0·3032 (9) | 6·5 |
| N(1) | 0·464 (1) | 0·625 (7) | −0·002 (2) | 2·5 |
| N(1′) | 0·285 (1) | 0·439 (7) | 0·489 (2) | 4·7 |
| N(2) | 0·428 (1) | 0·545 (6) | −0·184 (2) | 3·7 |
| N(2′) | 0·260 (1) | 0·181 (5) | 0·627 (3) | 3·4 |
| N(3) | 0·492 (1) | 0·871 (6) | −0·143 (3) | 4·3 |
| N(3′) | 0·324 (1) | 0·494 (7) | 0·645 (2) | 2·7 |
| C(1) | 0·373 (1) | 0·532 (7) | 0·087 (3) | 2·8 |
| C(1′) | 0·365 (1) | 0·467 (8) | 0·377 (3) | 4·3 |
| C(2) | 0·428 (1) | 0·411 (7) | 0·054 (2) | 2·7 |
| C(2′) | 0·316 (1) | 0·636 (7) | 0·424 (3) | 3·9 |
| C(3) | 0·461 (1) | 0·681 (7) | −0·107 (3) | 2·7 |
| C(3′) | 0·289 (1) | 0·323 (7) | 0·586 (3) | 1·8 |

* Fixed to determine origin.

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

Distances and angles involving primed atoms are in square brackets.

| | | |
|---|---|---|
| S(1)–C(1) | 1·63 (4) | [1·68 (4)] |
| N(1)–C(2) | 1·48 (5) | [1·43 (6)] |
| N(1)–C(3) | 1·33 (5) | [1·25 (5)] |
| N(2)–C(3) | 1·36 (5) | [1·27 (5)] |
| N(3)–C(3) | 1·23 (5) | [1·18 (5)] |
| C(1)–C(2) | 1·37 (5) | [1·45 (6)] |
| S(1)–S(1′) | 1·96 (2) | |
| C(2)–N(1)–C(3) | 126 (3) | [132 (4)] |
| S(1)–C(1)–C(2) | 123 (3) | [108 (3)] |
| N(1)–C(2)–C(1) | 106 (3) | [100 (3)] |
| N(1)–C(3)–N(2) | 128 (4) | [122 (4)] |
| N(1)–C(3)–N(3) | 120 (4) | [123 (4)] |
| N(2)–C(3)–N(3) | 112 (4) | [114 (4)] |
| S(1′)–S(1)–C(1) | 107 (2) | |
| S(1)–S(1′)–C(1′) | 112 (2) | |

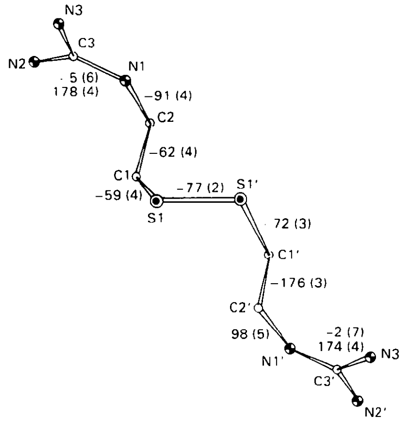

Fig. 1. Molecular conformation and atomic numbering used. The values with e.s.d.'s in parentheses are the torsion angles around respective bonds (°).

**Experimental.** Synthesized from AET (Hino, Tanaami, Yamada & Akaboshi, 1966*a*), and recrystallized from $H_2O$ to afford platelet shaped crystals; approximate dimensions 0·1 × 0·2 × 0·05 mm. Systematic absences corresponding to $0kl$, $l = 2n + 1$ and $h0l$, $h = 2n + 1$ observed on Weissenberg photographs. Rigaku automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 19 reflections with $11{\cdot}2° \leq 2\theta \leq 31{\cdot}0°$ used for determination of orientation matrix and cell dimensions. $D_m$ by flotation in $CH_2Br_2/C_6H_6$ mixture at 293 K. Diffraction data ($2\theta \leq 47°$) collected with $\omega$–$2\theta$ scan, scan speed 4° min$^{-1}$ ($2\theta$), and ($2\theta$) scan width $(1{\cdot}2 + 0{\cdot}35\tan\theta)°$ at 40 kV and 30 mA. 1114 independent reflections collected; 861 significant $[F_o \geq 3\sigma(F_o)]$ and used for structure determination and refinement. Three check reflections measured every 50 reflections showed no decay in intensity. Lorentz and polarization corrections, no absorption correction. Structure solved by Patterson and Fourier methods, and refined by block-diagonal least squares with anisotropic temperature factors. Positions of all H atoms were calculated geometrically and included in the structure factor calculations, but not in refinements. Final $R = 0{\cdot}087$ and $R_w = 0{\cdot}068$. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1{\cdot}0/[\sigma(F_o)^2 + 0{\cdot}0880|F_o| + 0{\cdot}0026|F_o|^2]$. Final difference map showed residual fluctuations from −0·95 to 0·72 e Å$^{-3}$ (especially close to the two Br atoms). All shifts in the parameters of non-H atoms were less than their e.s.d.'s in the final cycle. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All numerical calculations on an ACOS-1000 computer at the Computation Center of Osaka University using *The Universal Crystallographic Computing System* (1979).

**Discussion.** Table 1 gives the atomic coordinates of the non-H atoms, Table 2 the bond lengths and angles.* The molecular conformation with the atomic numbering is presented in Fig. 1.

Because of the existence of two heavy Br atoms, the quoted bond lengths and angles are not very accurate. However, the following dimensional characteristics of the GED molecule are observable: unlike the nearly equal guanidine C—N bond lengths observed in many other compounds such as arginine.HCl.$H_2O$ (Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970), arginine diethyl phosphate (Furberg & Solbakk, 1973), propylguanidinium diethyl phosphate (Furberg & Solbakk, 1972) and methylguanidinium dihydrogenorthophosphate (Cotton, Day, Hazen &

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* Lists of structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39080 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Larsen, 1973), C(3)—N(3) (1·23 Å) and C(3′)—N(3′) (1·18 Å) of this molecule are meaningfully shorter than C(3)—N(2) (1·36 Å) and C(3′)—N(2′) (1·27 Å), respectively, implying that neither guanidine group is in a full-resonance state. Furthermore, the difference Fourier map suggests protonation at N(2) and N(2′). On the other hand, S(1)—C(1) (1·63 Å) and S(1′)—C(1′) (1·68 Å) are within the double-bond range [1·71 (2) Å] (Kennard, 1968) and are slightly shorter than those found in other disulfide compounds such as L-cystine.2HCl (Peterson, Steinrauf & Jensen, 1960), L-cystine (Oughton & Harrison, 1959; Chaney & Steinrauf, 1974), *N,N′*-diglycyl-L-cystine (Yakel & Hughes, 1954) and L-cystinediamide.2HCl (Chaney & Steinrauf, 1968).

The torsion angles around the respective bonds are given in Fig. 1. The GED molecule consists of two chemically equivalent ethylguanidine groups on a central S—S bond and has no conformational symmetry. The most significant difference is observed in torsion angles C(1)—C(2)—N(1)—C(3) (−91°) and C(1′)—C(2′)—N(1′)—C(3′) (98°), and the angles S(1)—C(1)—C(2)—N(1) (−62°) and S(1′)—C(1′)—C(2′)—N(1′) (−176°) are also meaningfully different. The guanidine plane defined by the atoms N(1), C(3), N(2) and N(3) or N(1′), C(3′), N(2′) and N(3′) is roughly planar (r.m.s.d. 0·01 or 0·02 Å, respectively) with the displacement of the side-chain C(2) or C(2′) atom being −0·06 (7) or 0·09 (7) Å, respectively; the dihedral angle between the two planes is 5 (3)°.

The crystal structure viewed along the *b* axis is shown in Fig. 2. Possible hydrogen bonds and selected short contacts are listed in Table 3. The GED molecule takes an extended conformation, and is elongated along the *c* axis. Neighboring GED molecules are directly linked to each other by an N(3)···S(1′) hydrogen bond; also, the two Br atoms at the periphery of the GED molecules participate in hydrogen bonds and form short contacts with the N and C atoms of neighboring GED molecules, consequently stabilizing the crystal packing.

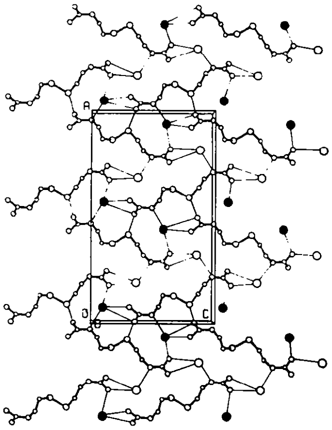

Fig. 2. Crystal packing viewed along the *b* axis. The thin lines represent possible hydrogen bonds. Filled and open circles show Br(1) and Br(2) atoms, respectively.

Table 3. *Possible hydrogen bonds and selected short contacts*

Hydrogen bonds

| Donor (at *x,y,z*) | Acceptor | Symmetry operation of acceptor | |
|---|---|---|---|
| N(1) | Br(1) | $1-x, 1-y, -0.5+z$ | 3·20 (3) Å |
| N(1′) | Br(2) | $0.5-x, y, -0.5+z$ | 3·15 (4) |
| N(2) | Br(1) | $x, 1+y, -1+z$ | 3·38 (3) |
| N(2′) | Br(2) | $x, y, z$ | 3·34 (3) |
| N(3) | Br(1) | $x, 1+y, -1+z$ | 3·45 (4) |
| N(3) | S(1′) | $1-x, 2-y, -0.5+z$ | 3·10 (4) |
| N(3′) | Br(1) | $x, 1+y, z$ | 3·34 (3) |
| N(3′) | Br(2) | $x, y, z$ | 3·56 (3) |

Short contacts (Br—C < 3·75; Br—N < 3·55; S—N < 3·45; S—C < 3·65; N—N < 3·10; C—C < 3·50 Å)

| Atom (1) (at *x, y, z*) | Atom (2) | Symmetry operation of atom (2) | |
|---|---|---|---|
| Br(1) | C(2) | $1-x, -y, 0.5+z$ | 3·45 (4) |
| Br(1) | N(3) | $1-x, 1-y, 0.5+z$ | 3·48 (4) |
| Br(2) | C(2′) | $0.5-x, -1+y, 0.5+z$ | 3·53 (4) |
| Br(2) | C(3) | $x, -1+y, 1+z$ | 3·61 (4) |
| Br(2) | N(2) | $x, y, 1+z$ | 3·45 (3) |
| Br(2) | C(2) | $x, y, 1+z$ | 3·69 (4) |
| S(1) | N(1) | $x, y, z$ | 3·02 (4) |
| S(1) | C(2) | $x, 1+y, z$ | 3·58 (4) |
| S(1′) | C(2) | $x, y, z$ | 3·36 (4) |
| S(1′) | N(3) | $1-x, 1-y, 0.5+z$ | 3·39 (4) |
| S(1′) | C(3) | $1-x, 1-y, 0.5+z$ | 3·37 (4) |
| N(2) | N(3′) | $x, y, -1+z$ | 3·09 (5) |
| C(1) | C(3′) | $0.5-x, y, -0.5+z$ | 3·49 (5) |

## References

Chaney, M. O. & Steinrauf, L. K. (1968). *Acta Cryst.* B**24**, 1564–1567.

Chaney, M. O. & Steinrauf, L. K. (1974). *Acta Cryst.* B**30**, 711–716.

Cotton, F. A., Day, V. W., Hazen, E. E. Jr & Larsen, S. (1973). *J. Am. Chem. Soc.* **95**, 4834–4840.

Crough, B. G. & Overman, R. R. (1957). *Science,* **125**, 1092.

Doherty, D. G. & Burnett, W. T. Jr (1955). *Proc. Soc. Exp. Biol. Med.* **89**, 312–314.

Doherty, D. G., Burnett, W. T. Jr & Shapira, R. (1957). *Radiat. Res.* **7**, 13–21.

Dow, J., Jensen, L. H., Mazumdar, S. K., Srinivasan, R. & Ramachandran, G. N. (1970). *Acta Cryst.* B**26**, 1662–1671.

Furberg, S. & Solbakk, J. (1972). *Acta Chem. Scand.* **26**, 3699–3707.

Furberg, S. & Solbakk, J. (1973). *Acta Chem. Scand.* **27**, 1226–1232.

Hanaki, A. & Akaboshi, S. (1966). *Jpn Anal.* **15**, 518–526.

Herve, A. & Bacq, Z. M. (1952). *J. Radiol. Electrol.* **33**, 651–655.

Hino, T., Tanaami, K., Yamada, K. & Akaboshi, S. (1966*a*). *Chem. Pharm. Bull.* **14**, 1193–1201.

Hino, T., Tanaami, K., Yamada, K. & Akaboshi, S. (1966*b*). *Chem. Pharm. Bull.* **14**, 1201–1209.

Inoue, M., Sakaki, T., Wakahara, A. & Tomita, K. (1978). *Biochim. Biophys. Acta,* **543**, 123–135.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–98. Birmingham: Kynoch Press.

Ishida, T., Shimizu, S., Inoue, M., Kitamura, K., Wakahara, A., Tomita, K. & Shinoda, M. (1981). *Bull. Chem. Soc. Jpn,* **54**, 1105–1107.

KENNARD, O. (1968). *International Tables for X-ray Crystallography*, Vol. III, p. 276. Birmingham: Kynoch Press (1983 reprint – Dordrecht, Holland: Reidel).
LANGENDORFF, H., KOCH, R. & HAGEN, U. (1954). *Strahlentherapie*, **95**, 238–250.
OUGHTON, B. M. & HARRISON, P. M. (1959). *Acta Cryst.* **12**, 396–404.
PATT, H. M., TYREE, E. B., STRAUBE, R. L. & SMITH, D. E. (1949). *Science*, **110**, 213–214.
PETERSON, J., STEINRAUF, L. K. & JENSEN, L. H. (1960). *Acta Cryst.* **13**, 104–109.
*The Universal Crystallographic Computing System* (1979). The Computation Center, Osaka Univ.
YAKEL, H. L. & HUGHES, E. W. (1954). *Acta Cryst.* **7**, 291–297.

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# The Monoclinic Structure of Tetracyanoethylene* (TCNE), $C_6N_4$, at 5, 150 and 295 K; Powder Diffraction Analysis

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**Abstract.** $M_r = 128{\cdot}1$, monoclinic, $P2_1/n$, $\lambda = 1{\cdot}909$ Å. At 5 K: $a = 7{\cdot}3313\,(7)$, $b = 6{\cdot}1108\,(4)$, $c = 6{\cdot}9315\,(4)$ Å, $\beta = 97{\cdot}043\,(5)°$, $V = 308{\cdot}19$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}380$ Mg m$^{-3}$, $R = 7{\cdot}4\%$ for $10 < 2\theta < 154{\cdot}4°$. At 150 K: $a = 7{\cdot}3860\,(12)$, $b = 6{\cdot}1449\,(9)$, $c = 6{\cdot}9548\,(9)$ Å, $\beta = 97{\cdot}138\,(11)°$, $V = 313{\cdot}2$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}358$ Mg m$^{-3}$, $R = 10{\cdot}0\%$ for $12 < 2\theta < 160°$. At 295 K: $a = 7{\cdot}501\,(6)$, $b = 6{\cdot}218\,(5)$, $c = 7{\cdot}004\,(6)$ Å, $\beta = 97{\cdot}22\,(5)°$, $V = 324{\cdot}1$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}312$ Mg m$^{-3}$, $R = 8{\cdot}5\%$ for $12 < 2\theta < 100°$. Structure refinements were made using the *EDINP* program and neutron powder diffraction data obtained on the D1A machine at the Institute Laue–Langevin, Grenoble. The accuracy of the 295 K data is poor, but agrees with X-ray results. The lower-temperature results suggest that the bond lengths in this monoclinic phase do not differ significantly from those in the cubic phase and that the central C=C bond is not anomalously short.

**Introduction.** The work presented here is part of a research programme to study the intermolecular forces in TCNE by way of lattice-dynamical measurements. Detailed neutron inelastic-scattering results from the monoclinic form of TCNE have already been published by Chaplot, Mierzejewski, Pawley, Lefebvre & Luty (1983), and the success of this experimental work depended in good measure on the quality of the lattice-dynamical calculation which was used both in the planning stage and in the analysis of the experimental results. In the preliminary work at 5 K it was clear that there was a considerable discrepancy between measured phonon inelastic-scattering cross-sections and those calculated with the structure determined at room temperature by Bekoe & Trueblood (1960, 1964). Use of the best-known structure for cross-section calculation is very important, and as the variation of the structure with temperature was not known it was most expedient for us to investigate this behaviour and, in particular, determine the structure at 5 K, the temperature where the phonon measurements are the most resolved. For this work the appropriate quality of result is given by neutron powder diffraction – phonon measurements are never made near Bragg points of very high Miller indices and therefore the highest accuracy obtainable by single-crystal studies is unnecessary here.

In the work which follows measurements were made at 150 and 295 K in addition to the work at 5 K in order to follow the changes in structural parameters with temperature, and to give a check on the accuracy of the powder diffraction method by performing a comparison with the conventional single-crystal X-ray structure determination.

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