

Molecular and Crystal Structure and IR Spectrum of 3,5-Dibromo-1,2,4-triazole

JUSSI VALKONEN,^a ILKKA PITKÄNEN^a and AARNE PAJUNEN

^a University of Jyväskylä, Department of Chemistry, SF-40100 Jyväskylä, Finland and

^b University of Helsinki, Department of Chemistry, SF-00100 Helsinki, Finland

3,5-Dibromo-1,2,4-triazole was synthesized by direct bromination of 1,2,4-triazole and recrystallized from water–ethanol solution. The compound crystallizes in the hexagonal space group $P\bar{6}2c$ with cell dimensions $a=11.697(2)$ Å and $c=6.791(2)$ Å.

The compound forms planar molecules, which are connected through hydrogen bonds. The IR spectra of the title compound and its deuterated form are reported and assigned.

The synthesis of halogenated triazoles is essentially known and their applications are generally familiar.^{1–6} By contrast, their structures and chemical behaviour have been little studied. The present structural research on 3,5-dibromo-1,2,4-triazole (abbrev. =Br₂trz) was undertaken as a continuation of earlier studies in this laboratory on the complex conformation of triazoles in aqueous solutions.^{7,8}

EXPERIMENTAL

Synthesis. The compound was synthesized by direct bromination of 1,2,4-triazole (abbrev. =trz) at room temperature.¹ Crystals for X-ray structure determination were recrystallized from water–ethanol (1:1) solution. The crystals were colourless needles. The deuterated compound was prepared by dissolving Br₂trz in a small amount of CH₃OD and precipitated by adding D₂O. This step was repeated five times, and the final product was analyzed with a mass-spectrometer to confirm that deuteration was successful. The density of the compound was determined by the flotation method with a mixture of C₆H₆ and CH₃I.⁹

X-ray data collection. Conditions for data collection are listed in Table 1. Unit cell dimensions were determined by least squares refinement. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

IR spectra. IR spectra were recorded on a Perkin-Elmer 283 Infrared spectrometer. The sample was finely ground and dispersed in a KBr pellet. The scan time was 12 or 24 min and the scan range from 4000 cm⁻¹ to 200 cm⁻¹. The resolution of the spectrometer is 7–1.5 cm⁻¹, depending on wavenumber.

CRYSTAL DATA

3,5-Dibromo-1,2,4-triazole, C₂HBr₂N₃, M.W.=226.86

Space group $P\bar{6}2c$ (No. 190), hexagonal

$a=11.697(2)$, $c=6.791(2)$ Å, $V=804.7(4)$ Å³

$Z=6$, $D_x=2.81$ g cm⁻³, $D_m=2.8$ g cm⁻³, $\mu(\text{MoK}\alpha)=148.3$ cm⁻¹

0302-4377/85 \$2.50

© 1985 Acta Chemica Scandinavica

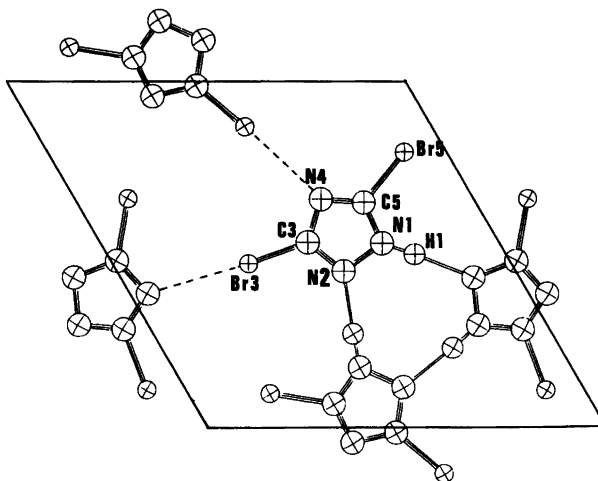
Table 1. Conditions of data collection for 3,5-dibromo-1,2,4-triazole.

	Diffractometer	Syntex P2 ₁
	Radiation	MoK α
	Monochromator	graphite crystal
	Crystal size (mm)	0.2×0.2×0.5
Unit cell determination	Number of reflections	15
	2 θ range (°)	15.72–15.75
Data collection	Temperature (°C)	23±1
	Collection method	2 θ / θ
	Scan speed (°/min)	1.5
	2 θ range (°)	6–70
	Number of reflections collected	764
	Number of independent reflections refined	293 ($I > 3 \sigma(I)$)
	<i>R</i>	0.038
	<i>R_w</i>	0.042

STRUCTURE DETERMINATION

According to the systematic absences the space group is $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$, but only space group $P\bar{6}2c$ gave the solution. The structure was solved with direct methods, using the program MULTAN.¹⁰ Multan gave the sites of bromine atoms, and the subsequent electron density map gave the sites of carbon and nitrogen atoms. A full matrix refinement was made, using unit weights for the structure factors. The scattering factors were those of Cromer and Mann.¹¹ Refinement of the structure, electron density calculations, and bond distance and angle calculations were made with the XRAY program.¹² The picture was drawn with the program ORTEP, which is a part of the XRAY system.

The final *R* value after refinement with isotropic temperature factors was 0.173, and after refinement with anisotropic temperature factors, 0.038. The highest peak in the electron

Fig. 1. Layered structure of 3,5-dibromo-1,2,4-triazole projected along the *c*-axis.

density difference map calculated after the final cycle of refinement was $0.5 \text{ e } \text{Å}^{-3}$. Lists of the structure factors and anisotropic thermal parameters are available from the authors on request.

RESULTS AND DISCUSSION

Structure. The positional parameters and temperature factors U_{eq} are listed in Table 2, and bond distances and angles in Table 3. A projection of one layer of the structure is shown in Fig. 1.

The molecule of Br_2trz is absolutely planar according to the space group symmetry. The z -coordinate is $\frac{1}{4}$ for all atoms, because they are in $6(h)$ positions. Refinement with a free z coordinate was also tested, but gave same solution.

Three molecules are joined together through hydrogen bonds between N(2) and N(1) atoms, and these triple molecules are connected through Br(3) and N(4) atoms. The system

Table 2. Fractional coordinates with estimated standard deviations in parentheses and temperature factors U_{eq} ($U_{\text{eq}} = 100 \cdot (U_{11}U_{22} + U_{33})/3$) for 3,5-dibromo-1,2,4-triazole.

Atom	x	y	z	U_{eq}
Br(3)	0.3394(1)	0.4723(1)	1/4	3.63
Br(5)	0.8915(2)	0.7944(1)	1/4	5.68
C(3)	0.5189(11)	0.5341(13)	1/4	2.70
C(5)	0.7167(15)	0.6491(13)	1/4	3.90
N(1)	0.7043(11)	0.5317(11)	1/4	3.59
N(2)	0.5668(14)	0.4507(13)	1/4	3.55
N(4)	0.6139(10)	0.6584(10)	1/4	2.97

Table 3. Interatomic distances (Å) and angles (°) with their standard deviations.

N(1)–N(2)	1.400(17)
N(2)–C(3)	1.346(26)
C(3)–N(4)	1.317(14)
N(4)–C(5)	1.261(23)
C(5)–N(1)	1.307(22)
Br(3)–C(3)	1.848(13)
Br(5)–C(5)	1.896(12)
N(1)–H(1) ^a	1.00
N(1)–N(2)–C(3)	105.3(11)
N(2)–C(3)–N(4)	111.9(12)
C(3)–N(4)–C(5)	102.6(13)
N(4)–C(5)–N(1)	118.8(11)
C(5)–N(1)–N(2)	101.4(14)
Br(3)–C(3)–N(2)	121.3(9)
Br(3)–C(3)–N(4)	126.8(13)
Br(5)–C(5)–N(1)	116.4(13)
Br(5)–C(5)–N(4)	124.8(12)
H(1)–N(1)–N(2) ^a	125.5
H(1)–N(1)–C(5) ^a	133.1

^a The site of hydrogen atom is not refined.

forms an infinite layer parallel to the *ab*-plane. The distance between layers is 3.40 Å.

There is a clear hydrogen bond N(1)–H(1)⋯N(2), with a nitrogen-nitrogen distance of 2.86 Å. The site of the hydrogen atoms was found from a difference Fourier map, but it could not be refined. Based on the unrefined site of the hydrogen atom, the N(1)–H(1) distance is 1.00 Å, the H(1)⋯N(2) distance 1.85 Å and the angle N(1)–H(1)⋯N(2) 177°.

There is also interaction between Br(3) and N(4), since the distance between these atoms is 3.07 Å, which is shorter than the sum 3.45 Å of the Van der Waals radii of bromine and nitrogen. The results are in good agreement with those for trz.^{13–15} Both molecules are planar, and there is only a small variation in bond lengths. The bonds C(3)–N(4) and C(5)–N(4) are shorter the bond between N(1) and N(2) is longer in Br₂trz than in trz. The influence of the bromine atoms is also seen in the ring angles N(2)–C(3)–N(4) and N(4)–C(5)–N(1), which are larger than other angles in the ring.

Goldstein *et al.*¹⁴ describe five different resonance forms for trz. In Br₂trz one double bond can be localized between C(5) and N(4) because of the short bond length of 1.26 Å, but the site of the second double bond is not clear; it is probably distributed over the ring.

IR SPECTRA

The vibrational spectra of triazole and its 3-chloro derivative have been thoroughly studied.^{16–20} Grinsteins *et al.* have earlier studied Br₂trz and its D, Ag and K derivatives.¹⁸ Our purpose is to assign the IR-spectra of Br₂trz, with the aid of assignments given in the literature for related trz compounds and the crystal structure of Br₂trz.

Like 1H-trz, the title compound is of the C_s tautomeric form. There are 18 fundamentals, represented by $\Gamma = 13A' + 5A''$. The vibrations belonging to A' are 5 ring stretchings (R₁–R₅), 2 ring bendings (R₆–R₇), 1 $\nu(\text{NH})$, 2 $\nu(\text{CBr})$, 1 $\delta(\text{NH})$ (bending in plane) and 2 $\delta(\text{CBr})$; correspondingly, A'' has 2 ring torsions (R₈–R₉), 1 $\gamma(\text{NH})$ (out of plane) and 2 $\gamma(\text{CBr})$. Observed frequencies and relative peak heights for the infrared spectra of Br₂trz and Br₂trz-*d*₁ in KBr at room temperature are given in Table 4 together with suggested assignments. Eleven A' vibrations and four A'' vibrations were found. The three missing vibrations presumably coincide with others.

Ring Vibrations. Five-membered ring compounds with two double bonds have nine ring vibrations. All are infrared active when the symmetry is C_s.

There are bands at wavenumbers 1275, 1252 and 1130 cm⁻¹, which correspond mainly to R₄ (ring stretching), $\delta(\text{NH})$ (bending), and R₅ (ring breathing). This deduction is based on a comparison of the IR-spectra recorded for Br₂trz, Br₂trz-*d*₁, trz¹⁶ and Cltrz.^{19,20} According to Grinstein *et al.*¹⁸ the first and second are ring vibrations but the third is not explained; they supposed that $\delta(\text{NH})$ might be found at lower wavenumbers. Vibrations have been named on the basis of the dominant contribution: all vibrations are mixed.

Comparison of the ring vibrations of Br₂trz with those of trz under the same conditions shows the frequencies to be generally near each other. The ring vibrations are typical for C_s-symmetrical triazoles and other heteroaromatic five-membered ring compounds with two double bonds.²¹ When the symmetry is C_{2v}, one ring torsion is not IR active.

NH Vibrations. The NH stretching absorption band is very strong and broad, 3200–2400 cm⁻¹, in the solid state and contains many sub-bands in this region. The main features of the $\nu(\text{NH})$ band structure can be explained by binary overtones and combinations in Fermi resonance with the NH stretching fundamental. Six fundamentals in the 1550–1100 cm⁻¹

Table 4. Observed frequencies (cm^{-1}) and assignments in the infrared spectra of solid Br_2trz and $\text{Br}_2\text{trz}-d_1$ in KBr at 20°C .^a

Br_2trz	$\text{Br}_2\text{trz}-d_1$	H/D	Assignment and description	
			Symmetry	Mode
3200–2400				
3101 s	3102 m			
2960 sh	2960 sh			
2908 s	2902 m	1.27 ^b	A'	$\nu(\text{NH})$ and/or associated
2790 sh	2775 sh			
2745 s	2744 m			
	2541 w			
2450–1950				
2410 w				
	2370 sh			
	2339 m			
	2306 m		A'	$\nu(\text{ND})$ and/or associated
2235 vw	2225 s			
	2175 sh			
	1975 w			
	1915 w			
1613 m				overtone 2 $\gamma(\text{NH})$
1535 m	1250 sh			comb. $\gamma(\text{NH}) + \text{R}_8/\gamma(\text{ND}) + \text{R}_8$
1516 m	1514 m		A'	R_1 ring stretching
1428 vs	1433 vs		A'	R_2 ring stretching
	1402 m			comb. $\delta(\text{ND}) + \nu(\text{CBr})$
	1395 m			overtone 2R_8
1342 m	1366 m		A'	R_3 ring stretching
1275 vs	1270 vs		A'	R_4 ring stretching
1252 s	1013 s	1.24	A'	$\delta(\text{NH})/\delta(\text{ND})$
1130 m	1150 m		A'	R_5 ring breathing
	1038 m			comb. $\gamma(\text{ND}) + \nu(\text{CBr})$
1013 vs	975 vs	1.04	A'	R_6 ring bending
985 m	941 s	1.05	A'	R_7 ring bending
831 m	595 m	1.40	A''	$\gamma(\text{NH})/\gamma(\text{ND})$, out of plane
699 m	698 m		A''	R_8 ring torsion
650 w	658 w		A''	R_9 ring torsion
464 m	460 m		A'	$\nu(\text{CBr})$
363 m	354 m		A'	$\delta(\text{CBr})$
310 w	308 w		A''	$\gamma(\text{CBr})$

^a vs, s, m, w and sh mean very strong, strong, medium, weak and shoulder respectively. ^b Calculated approximate band middle (2800 and 2200 cm^{-1}).

region can give rise to 21 binary overtones and combinations between 3100- and 2200 cm^{-1} , which coincides with the NH stretching band region.

The $\nu(\text{NH})/\nu(\text{ND})$ frequency ratio has a mean value of 1.27, whereas the value calculated from Hooke's law is 1.37. One cause of the discrepancy is the interaction or coupling with another vibration. The main cause, however, is the unusually high anharmonicity of the NH stretching vibration due to strong hydrogen bonding, $\text{N-H}\cdots\text{N}$. The same situation is found in trz, and it is in agreement with the crystal structure of Br_2trz .

The $\delta(\text{NH})$ -in-plane bending vibration is not localized; it is distributed mainly among 1275 and 1252 cm^{-1} wavenumbers, the last being dominantly $\delta(\text{NH})$ mode. Upon deuteration

new bands appeared at 1038 and 1013 cm^{-1} . The former is possibly a combination of $\gamma(\text{ND}) + \nu(\text{CBr})$ and the latter is $\delta(\text{ND})$ (bending n plane): $\delta(\text{NH})/\delta(\text{ND})$ is 1.24, 1.18, and 1.15 for Br_2trz , trz^{17} and Cltrz ,²⁰ respectively.

$\gamma(\text{NH})$ (out of plane) and $\gamma(\text{ND})$ yield broad bands of medium intensity at 836 and 602 cm^{-1} . The strong hydrogen bonds influence greatly the NH frequencies of Br_2trz in the solid state.

CBr Vibrations. Obviously $\nu(\text{CBr})$ (467 cm^{-1}), $\delta(\text{CBr})$ (365 cm^{-1}) and $\gamma(\text{CBr})$ (310 cm^{-1}) coincide with others or double bands. Because Br is a heavy atom, the NH group does not have a great effect on the vibrations of C–Br, as correspondingly it does not have a great effect on the vibrations of C–Cl in Cltrz . Thus the frequencies of the pairs of C–Br vibrations are nearly equal, and the molecule in this sense behaves as if it had C_{2v} -symmetry. Although according to the crystal structure study the ring is not a regular five-membered one, and Br(3) is in weak interaction with N(4) of a neighbouring molecule, these factors clearly do not have a great influence on the C–Br vibrations. The peak of $\delta(\text{CBr})$ has a shoulder, and the peak of $\gamma(\text{CBr})$ is blunt-ended.

Several very weak bands were observed in the spectra in addition to those listed in Table 3. These are believed to be due to overtones and combinations. The lattice vibrations are below 200 cm^{-1} .

REFERENCES

1. Kröger, C.-F. and Miethchen, R. *Chem. Ber.* 100 (1967) 2250.
2. Becker, H., Wehner, K. and Eisenschmidt, V. *Brit. Pat.* 1, 123, 947 (1968).
3. Becker, H.G.O., Eisenschmidt, V. and Wehner, K. *Ger. Pat.* 60, 762 (1968).
4. Grinstein, V.Ya. and Strazdina, A. *Khim. Geterotsikl. Soedin.* 5 (1969) 1114.
5. Becker, H.G.O. and Ebisch, R. *J. Prakt. Chem.* 314 (1972) 923.
6. Miethchen, R., Albrecht, H. and Rachow, E. *Z. Chem.* 10 (1970) 220.
7. Lumme, P. and Pitkänen, I. *Acta Chem. Scand. A* 28 (1974) 1106.
8. Pitkänen, I. *Research Report No. 8*, Department of Chemistry, University of Jyväskylä, Jyväskylä 1980.
9. Midgley, H.G. *Acta Cryst.* 4 (1951) 565.
10. Main, P., Fiske, S.J., Hull, S.E., Lessinger, L., Germain, G., Declercq, J.-P. and Woofson, M.M. *MULTAN 80: A System for Automatic Solution of Crystal Structure for X-Ray Diffraction Data*, University of York, York 1980.
11. Cromer, D.T. and Mann, J.B. *Acta Crystallogr. A* 24 (1968) 321.
12. Stewart, J.M. *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
13. Jeffrey, G.A., Ruble, J.R. and Yates, J.H. *Acta Crystallogr. B* 39 (1983) 388.
14. Goldstein, P., Ladell, J. and Abowitz, G. *Acta Crystallogr. B* 25 (1969) 135.
15. Deuschl, H. *Ber. Bunsenges. Phys. Chem.* 69 (1965) 550.
16. Bougeard, D., Le Calvé, N., Saint Roch, B. and Novak, A. *J. Chem. Phys.* 64 (1976) 5152.
17. Faniran, J.A. and Bertie, J.E. *J. Chem. Soc. Faraday Trans. 2*, 9 (1977) 1272.
18. Grinstein, V.Ya., Strazdina, A.A. and Grinvalde, A.K. *Khim. Geterotsikl. Soedin.* 6 (1970) 248.
19. Saidi-Idrissi, M., Senechal, M., Sauvaitre, H., Cotrait, M. and Garrigou-Lagrange, C. *J. Chim. Phys.* 77 (1980) 195.
20. Saidi-Idrissi, M., Garrigou-Lagrange, C. and Pouchan, C. *Can. J. Chem.* 59 (1981) 3341.
21. Katritzky, A.R. *Quart. Rev.* 13 (1959) 353.

Received April 10, 1985.