X-Ray Crystal and Molecular Structure of 'Tetrazene', ('Tetracene'), $C_2H_8N_{10}O$

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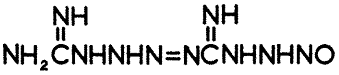
Summary The primary explosive tetrazene exists in the solid state as the zwitterion (guanidinium) form of 1-amino-1-[(1*H*-tetrazol-5-yl)azo]guanidine hydrate; the A and B crystal modifications have the same molecular conformation and are related as polymorphs.

TETRAZENE (I) was first assigned[1] the structure (II); structure (III) was suggested[2] following a re-investigation. (I) has now been examined by *X*-ray crystallographic methods using Cu-radiation data collected with a Hilger and Watts four-circle diffractometer. The three compounds which were investigated are shown in the Table; the structure parameters have been refined by anisotropic least-squares methods, and in each case all hydrogen atoms were located and their positional and thermal parameters were included in the refinement.

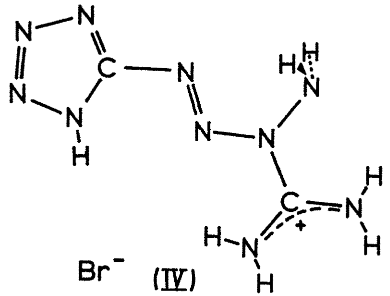


$\mathrm{NH_2}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{NHNHN{=}N}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{NHNHNO}$

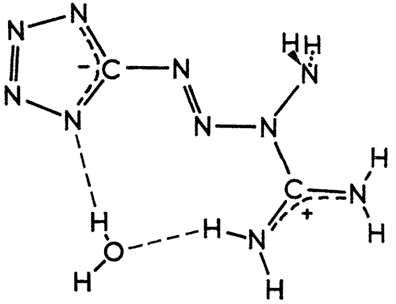
(II)

(III)

(I) forms compounds with strong acids and in order to establish directly the arrangement of the organic ion, the structure of the hydrobromide was first determined by the heavy-atom method; it may be represented formally as (IV), 1-amino-1-[(1*H*-tetrazol-5-yl)azo]guanidinium bromide, but the values of bond lengths (Figure 1) and angles[3] show that this represents an idealization of the bonding scheme. The molecule is approximately planar with the exception of the hydrogen atoms of the 1-amino-group, which has a pyramidal conformation with one hydrogen atom above the molecular plane and one below, the nitrogen lone pair of electrons being directed towards the guanidinium group.



(IV)



(V)

Two crystalline modifications of (I) are known;[4] the structure of the A-form was solved by a Patterson method and the structure of the B-form was then derived in a direct way on the basis of observed relationships between the *X*-ray intensities of the two forms. The molecular dimensions in the two crystals are closely similar (Figure 2); the oxygen atom is present as a hydrogen-bonded water molecule and the molecular structure may be represented as (V), the zwitterion (guanidinium) form of 1-amino-1-[(1*H*-tetrazol-5-yl)azo]guanidine hydrate, but as in the case of the bromide, the values of bond lengths and angles for the A[5] and B[5] structures show that this formal description is an idealization of the bonding scheme. The conformation of the 1-amino-group is the same as that found in the bromide, but the tetrazole ring does not carry a proton, in contrast to the situation in the bromide where salt formation is brought about by protonation of the tetrazole ring at position 1. All three structures include a substituted planar guanidinium grouping.

Crystals of the A- and B-forms of (I) contain approximately planar sheets of molecules, the arrangements within the sheets being closely similar in the two forms; an extensive system of hydrogen bonds links the molecules within sheets. The two forms differ mainly in the relationship between neighbouring sheets of molecules and the resulting interactions between molecules in neighbouring sheets; they are related as polymorphs, but there are special features about the relationship which will be discussed elsewhere.[5]

The mechanism suggested[2] for the formation of (I) by the reaction of sodium nitrite and an aminoguanidinium salt in neutral solution involves the reaction of tetrazole-5-diazonium ion, formed as an intermediate, with unchanged aminoguanidine; the revised structure now presented for (I) supports this view of the course of the reaction, but the position of coupling is normal rather than abnormal as previously suggested, since it is observed[6] in other cases that such coupling reactions involving substituted hydrazines usually occur at the substituted nitrogen atom rather than the unsubstituted one.

Crystal data for the compounds under investigation

Compound	Space group		Lattice parameters					No. of reflections	Present value of R	Bond[a] e.s.d.'s (Å)
		a (Å)	b (Å)	c (Å)	β (°)	D_c (g cm^{-3})	D_m (g cm^{-3})			
Tetrazene hydrobromide	$P2_1/a$	15·6902	6·7469	9·2748	111·094	1·891	1·892	1507	0·034	0·004
$C_2H_7N_{10}Br$		(11)	(6)	(7)	(6)					−0·007
A-Tetrazene	$P2_1/a$	12·955	9·295	6·847	111·54	1·629	1·628	1588	0·046	0·002
$C_2H_8N_{10}O$		(2)	(1)	(1)	(1)					−0·003
B-Tetrazene	Ia	12·888	9·332	6·811	112·47	1·651	1·653	776	0·026	0·005
$C_2H_8N_{10}O$		(1)	(1)	(1)	(1)					−0·009

(e.s.d.'s in parentheses)

[a] For bonds involving C and N atoms, from least-squares analysis.

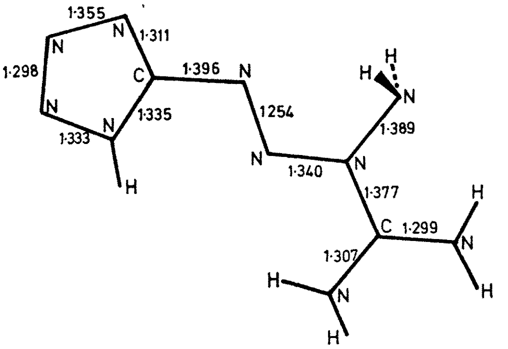


FIGURE 1. *Bond lengths (Å) in tetrazene hydrobromide.*

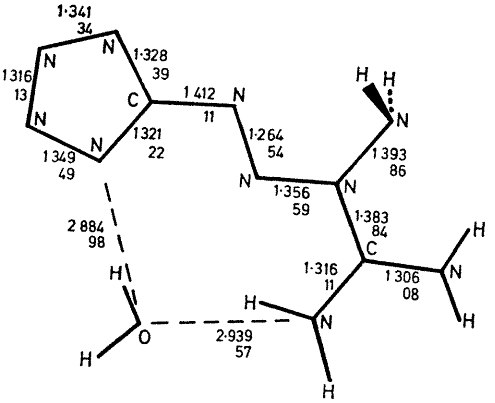


FIGURE 2. *Bond lengths (Å) in A-tetrazene (upper figures) and B-tetrazene (lower figures).*

The B-form of (I) is the product of reaction at temperatures below approximately 60°; above this temperature the A-form appears.[7] In contact with water at ambient temperatures the B-form transforms very slowly to the A-form, and the latter must therefore be regarded as the thermodynamically stable form under these conditions.

(*Received, October 5th,* 1970; *Com.* 1706.)

[1] K. A. Hofmann and R. Roth, *Ber.*, 1910, **43**, 682; K. A. Hofmann, H. Hock, and R. Roth, *ibid.*, p. 1087; K. A. Hofmann and H. Hock, *ibid.*, 1911, **44**, 2946; K. A. Hofmann, H. Hock, and K. Kirmreuther, *Annalen*, 1911, **380**, 131.

[2] S. H. Patinkin, J. P. Horwitz, and E. Lieber, *J. Amer. Chem. Soc.*, 1954, **77**, 562.

[3] B. W. Clements and J. R. C. Duke, to be submitted for publication in *Acta Cryst.*

[4] J. R. C. Duke, Ministry of Supply unpublished reports, 1955.

[5] B. W. Clements and J. R. C. Duke, to be submitted for publication in *Acta Cryst.*

[6] P. A. S. Smith, "Open Chain Nitrogen Compounds," vol. II, Benjamin, New York, 1966, pp. 130, 345; I. T. Millar and H. D. Springall, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, London, 1966, p. 610.

[7] B. P. 985,293/1960.