

A Re-investigation of the Structure of 2,2',2''-Triamino-triethylamine-trihydrochloride

RITA GRØNBÆK HAZELL and
SVEND ERIK RASMUSSEN

Department of Inorganic Chemistry,
University of Aarhus, Aarhus C, Denmark

The structure of 2,2',2''-triamino-triethylamine-trihydrochloride, "trenhydrochloride", was reported earlier.¹ For lack of computer facilities anisotropic temperature factor parameters were not employed at that time, and it was anticipated that further refinement might lead to slightly changed dimensions of the molecule.

In fact later refinement including anisotropic vibration parameters did lower the *R*-value from 14% to 12% with no significant change of atomic positions, and it became obvious that some systematic errors in the data prevented further progress. It appeared that the weak, visually estimated intensities had generally been overestimated although the agreement between visually and photometrically estimated intensities had earlier been considered good.¹ The conclusion was reached that whereas the visual data alone were probably quite good, and the photometric data alone were even better, the scaling between the two sets of data had not been successful probably because least squares methods were not applied. It is believed that the two sets separately could have been refined to somewhat lower *R*-values, but the temperature factor parameters might have been different.

When an automatic diffractometer of the Arndt-Phillips² type became available to us a set of data within a sphere of reflection of radius $\sin\theta/\lambda = 0.72$ was collected using Mo-radiation, balanced filters and a scintillation counter with pulse height discrimination. One fourth of the reciprocal lattice was recorded, giving 6 equivalent measurements for general reflexions. 675 independent reflexions were recorded. 156 of these had $I < 2.5 \cdot \sigma I$ and were left out of the refinements. The crystal was ground roughly spherical of a diameter of 0.4 mm. No absorption correction was applied.

The new data gave *R* = 8% when the old parameters were used. After a few cycles of block-diagonal least squares re-

finement a difference Fourier map was calculated which showed the hydrogen atoms bonded to the carbon atoms at the positions calculated and also showed some peaks around the nitrogen atoms. Three positions were chosen which gave reasonable distances to the nitrogen atom and to one another; these points were fairly close to the lines from nitrogen to the three nearest chlorine atoms. This arrangement

Table 1. Coordinates in fractions of the unit cell; standard deviations $\times 10^4$ in parentheses. Isotropic temperature factor parameters *U* in $\text{Å}^2 \times 10^{-4}$.

	x	ox	y	oy	z	oz	U	ou
C ₁	.2021	(1)	.2021	(1)	.2021	(1)		
C ₂	.4392	(1)	.4392	(1)	.4392	(1)		
C ₃	.9315	(1)	.9315	(1)	.9315	(1)		
N _t	.7344	(2)	.7344	(2)	.7344	(2)		
N _p	.7540	(3)	.7147	(3)	.0061	(2)		
C ₁	.6570	(3)	.6539	(3)	.8114	(3)		
C ₂	.7195	(3)	.6124	(3)	.9267	(3)		
H ₁₁	.1274	(30)	.9228	(36)	.2350	(29)	306	(104)
H ₁₂	.0759	(40)	.7803	(38)	.1567	(35)	479	(118)
H ₂₁	.3055	(45)	.9326	(34)	.0962	(40)	539	(125)
H ₂₂	.1695	(31)	.9490	(29)	.0328	(29)	187	(100)
H ₁	.2009	(34)	.4292	(37)	.1979	(35)	413	(115)
H ₂	.2830	(45)	.4879	(38)	.2943	(47)	807	(177)
H ₃	.2550	(41)	.5235	(38)	.1712	(40)	639	(142)

	Anisotropic temperature factor parameters, u_{ij} , in $\text{Å}^2 \times 10^{-4}$.					
	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
C ₁	441	(3)	441	(3)	-102	(8)
C ₂	563	(4)	563	(4)	5	(10)
C ₃	598	(4)	598	(4)	-227	(10)
N _t	316	(11)	316	(11)	20	(20)
N _p	900	(27)	571	(20)	380	(16)
C ₁	527	(20)	513	(19)	506	(20)
C ₂	482	(32)	410	(16)	492	(19)

Table 2. Interatomic distances, bond angles and torsion angles.

	Uncorrected	Corrected for riding motion assuming second atom "rides" on first	
N _t - C ₁	1.474 (4)	1.492	
C ₁ - C ₂	1.495 (5)	1.498	
C ₂ - N _p	1.457 (5)	1.474	
C ₁ - H ₁₁	1.027 (37)		
C ₁ - H ₁₂	1.187 (42)		
C ₂ - H ₂₁	1.084 (46)		
C ₂ - H ₂₂	0.967 (33)		
N _p - H ₁	0.889 (38)		
N _p - H ₂	0.911 (44)		
N _p - H ₃	0.978 (45)		
		Angles in degrees	
		C ₁ - N _t - C ₁	108.8 (3)
		N _t - C ₁ - C ₂	113.3 (3)
		C ₁ - C ₂ - N _p	112.6 (3)
		Torsion angles in degrees	
		C ₁ - N _t - C ₁ - C ₂	-155.6
		N _t - C ₁ - C ₂ - N _p	60.7
N _p - C ₁	3.211 (4)		
N _p - C ₂	3.274 (3)		
N _p - C ₃	3.151 (3)		

Table 3. Observed and calculated structure factors.

Table with 48 columns: h, k, l, Fobs, Fcalc, Phase, and 40 columns of h, k, l, Fobs, Fcalc, Phase. The table lists observed and calculated structure factors for various h, k, l indices.

gives an approximately staggered configuration around the C—N bond, and the hydrogen atoms all appear at small peaks in the difference map although other peaks of at least similar height can also be found, especially close to the chlorine atoms. The *R*-value dropped when the hydrogen atoms were inserted and further refinement brought it down to 4.76 %. Hydrogen atom coordinates and isotropic temperature factors were allowed to refine but all stayed close to the values at which they were inserted.

The standard deviations from the counting statistics, $\sigma(F^2)_{\text{count}}$, were found not to account for all errors, but had to be modified by a term proportional to the intensity: $\sigma(F^2) = \sigma(F^2)_{\text{count}} + kF^2$. The weights for the least squares refinement were then: $w = 1/(\sigma F)^2$;

$$\sigma F^2 = \sqrt{F^2 + \sigma(F^2)} - F;$$

the constant *k* (0.04) was adjusted so that the average of $w||F_o| - |F_c||^2$ was nearly independent of the size of *F*. The programs used were G3³ for the least squares refinement, G4⁴ for data reduction and ORFFE⁵ for correction of bond lengths for thermal vibration effects.

Geometric and thermal parameters are given in Table 1, bond lengths and angles in Table 2 and structure factors in Table 3.

The difference between $N_t - C_1(x_1)$ and $N_p - C_2(x_2)$ is 0.017 Å using uncorrected distances and 0.018 Å using distances corrected for thermal vibration effects. We can reasonably assume that other systematic errors influence the two bond length determinations in similar ways. The quotient $t = (x_1 - x_2)/(\sigma_{x_1}^2 + \sigma_{x_2}^2)^{1/2}$ is 2.66. With 519 observations we assume that the number of degrees of freedom is infinite, thus the probability is only 1 % that *t* should exceed 2.58. We can at this significance level reject the hypothesis that the two bond lengths are equal. Since the primary nitrogen atoms are protonized their N—C distances are probably a little longer than they are in the free amine. This supports the hypothesis that nitrogen-carbon distances in aliphatic compounds

are greater for tertiary nitrogen atoms than for primary ones.

The C₁—C₂ distance, 1.495 Å, differs significantly from the C—C distance 1.54 Å in paraffinic compounds. The contraction which takes place in bond length when a nitrogen atom replaces a carbon atom in an aliphatic chain appears to effect the carbon-carbon distance.

The mean of the four C—H distances is 1.07 Å, $\sigma = 0.05$ Å. This compares favourably with a tabulated average of 1.073 Å for di-substituted carbon.⁶ The average of the three N—H distances is 0.93 Å, $\sigma = 0.04$ Å to be compared with a tabulated value of 0.99 Å for N—H bonds next to C—N linkages.⁶ Although the C—H and N—H bond lengths exhibit a rather large scatter the difference between their means is significant at the 5 % level and is in agreement with trends obtained from more accurate methods.

Comparison with the earlier less accurate determination shows that the new bond length determinations differ from 1 σ to 2.5 σ from the previous determination using the earlier larger standard deviations. The new standard deviations are one fifth of the previous ones.

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