1,6-Diazabicyclo[4.4.4]tetradecane and its Inside-protonated Ion: Changes in Space Groups

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The crystal structures of 1,6-diazabicyclo[4.4.4]tetradecane (**1**) and of its inside-protonated ion (**2**), which were originally described in space group $C2/c$, should be described instead in trigonal space groups, (**1**) in $R\bar{3}c$ and (**2**) in $P\bar{3}1c$; both moieties have crystallographically imposed point symmetry D_3 rather than C_2.

Recently, the crystal structures of the bicyclic compound 1,6-diazabicyclo[4.4.4]tetradecane (**1**) and of its inside-protonated ion (as the chloride salt) (**2**) have been described.[1] Both compounds were reported as monoclinic, space group $C2/c$, with the molecules (or ions) lying on sites of C_2 symmetry. In fact, both structures should be formulated in trigonal space groups with molecular point symmetry D_3.

Compound (**1**). The reported cell dimensions are: $a = 12.266(7)$, $b = 11.817(8)$, $c = 8.520(5)$ Å, $\beta = 92.64(5)°$, $Z = 4$. The vectors $\frac{1}{2}(\mathbf{a} + \mathbf{b})$, $\frac{1}{2}(\mathbf{a}-\mathbf{b})$, $-\mathbf{c}$ describe an effectively rhombohedral unit cell with $a_r = b_r = 8.516$, c_r $(=c) = 8.520$ Å, $\alpha_r = \beta_r = 88.10$, $\gamma_r = 87.86°$, $Z = 2$. Conclusive proof of the trigonal symmetry comes from the atom co-ordinates† which, when transformed according to the relations $x_r = x + y - \frac{1}{2}$, $y_r = x - y$, $z_r = \frac{1}{2} - z$, yield values that are compatible with space group $R\bar{3}c$ within the reported e.s.d.s.‡

Compound (**2**). The reported cell dimensions are: $a = 8.233(4)$, $b = 14.261(7)$, $c = 10.671(5)$ Å, $\beta =$

† The atomic co-ordinates were obtained from the Crystallographic Data Centre, Cambridge. Co-ordinates of the methylene hydrogen atoms were not included.

‡ The translational components of $\frac{1}{2}$ are necessary to place the origin at the conventional centre of symmetry.

90.05(4)°, $Z = 4$. The same vectors as before, $\frac{1}{2}(\mathbf{a} + \mathbf{b})$, $\frac{1}{2}(\mathbf{a} - \mathbf{b})$, $-\mathbf{c}$, describe a hexagonal cell with $a_h = b_h = 8.233$, $c_h = 10.671$ Å, $\alpha_h = \beta_h = 89.98°$, $\gamma_h = 120.00°$. The co-ordinate transformations $x_h = x + y$, $y_h = x - y$, $z_h = -z$ yield values that are compatible with space group $P\bar{3}1c$.§¶

Since the co-ordinate shifts necessary to achieve the higher symmetries are no greater than the reported e.s.d.s, the changes in space group do not change the descriptions of the structures other than to introduce exact, crystallographic, symmetry elements in place of approximate ones. Thus, the bicyclic moieties in both compounds have crystallographic symmetry D_3, rather than the C_2 imposed by the monoclinic descriptions. Potential D_3 symmetry was shown by spectroscopic measurements.[2]

There are numerous examples in the literature of crystallographic studies that are based on space groups of unnecessarily low symmetry. In some cases, such as the present ones, the exact symmetries of molecular species may go unrecognized; in other instances, severe errors in bond lengths and angles may result.[3] We urge that workers in the field remain continually alert to the problem of describing a structure in the most appropriate space group.

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§ The atomic co-ordinates for the structures reported here are available on request from The Director, Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ *Added in proof:* Dr. Orpen has confirmed that least-squares refinements of the structures of (**1**) and (**2**)·Cl in the amended space groups proceed smoothly yielding residuals, R, of 0.050 and 0.031, for the 316 and 253 unique observed data, respectively. The *molecular* structures of (**1**) and (**2**) are identical within experimental error to those reported in ref. 1. The refined co-ordinates have been deposited with the Cambridge Crystallographic Data Centre.

References

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3 V. Schomaker and R. E. Marsh, *Acta Crystallogr., Sect. B*, 1979, **35**, 1933; O. Ermer and J. D. Dunitz, *Acta Crystallogr., Sect. A*, 1970, **26**, 163.