Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A novel benzylated carboxytriazole: 1-benzyl-4-carboxybenzotriazole

Graham Smith,* Steven E. Bottle, Damien A. Reid, D. Paul Schweinsberg and Raymond C. Bott

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia

Correspondence e-mail: g.smith@qut.edu.au

Received 19 March 2001
Accepted 15 May 2001
Online 22 May 2001

The crystal structure of the novel title benzylated carboxytriazole, $C_{14}H_{11}N_3O_2$, having potential as a corrosion inhibitor for copper and copper-based alloys, confirms that the site of the benzyl substituent is on the triazole ring nitrogen which is *trans*-related rather than *cis*-related to the carboxylic acid group. The molecules participate in asymmetric intermolecular hydrogen-bonding interactions involving the carboxylic acid H atom and two of the triazole N atoms [O···N 2.683 (5) and 3.413 (5) Å], giving rise to a chain polymer.

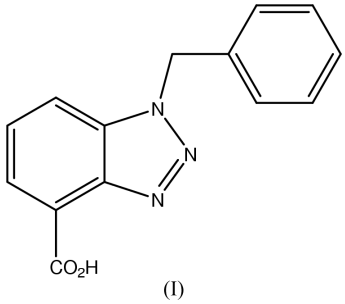
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
R factor = 0.042
wR factor = 0.102
Data-to-parameter ratio = 7.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Benzotriazole (BTAH) has been used successfully for the prevention of copper corrosion under both atmospheric and immersed conditions. In the latter case, very high inhibition efficiency (Cotton, 1963; Mansfeld *et al.*, 1971) is observed due to the formation of a polymeric BTA–Cu–BTA–Cu film in neutral and alkaline conditions. However, in acidic corrosive environments this efficiency is decreased (Xue *et al.*, 1991). BTAH derivatives may offer higher inhibition efficiencies than the parent molecule, with steric effects giving better surface coverage of the metal. The inhibitive effects of 5-alkyl derivatives of benzotriazole and the 4- and 5-carboxybenzotriazole in various aqueous solutions have been studied (Frignani *et al.*, 1999; Wu & Nobe, 1981; Otieno-Alego *et al.*, 1999; Huynh *et al.*, 2000). In an effort to further refine our understanding of the mechanism of corrosion inhibition of the carboxybenzotriazoles, a novel benzylated carboxytriazole 1-benzyl-4-carboxybenzotriazole (BCBTAH), (I) (Fig. 1), which cannot form the polymeric copper film implicated in inhibitions in neutral and alkaline corrosive environments was synthesized. To validate and correlate molecular modelling studies with established corrosion efficiencies, the absolute position of the benzyl group relative to the carboxylic acid group was determined using single-crystal X-ray crystallography.



(I)

The analysis established that the benzyl group is attached to the triazole nitrogen (N1) which is *trans*-related to the

© 2001 International Union of Crystallography
Printed in Great Britain – all rights reserved

carboxylic acid group rather than to the adjacent (*cis*-related) ring nitrogen (N3). The carboxylic acid group is almost coplanar with the benzotriazole ring [torsion angle C9—C4—C41—O41 −165.8 (4)°], while the benzyl group is synclinally related [N2—N1—C10—C11 −75.9 (5)°]. Packing in the unit cell shows no intramolecular interactions between this triazole nitrogen and the adjacent carboylate group. However, a chain polymer is formed through an asymmetric three-centre intermolecular hydrogen-bonding association between the carboxylic acid H atom of one molecule, and the non-substituted hetero–N atoms of a second molecule: one strong [O41—H41···N3^{i} 2.683 (5) Å and O—H···N 152 (6)°] and the other weak [O41—H41···N2^{i} 3.413 (5) Å and O—H···N 145 (4)°] [symmetry code: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$].

Experimental

The title compound was synthesized by refluxing a solution of 4-carboxy-1*H*-benzotriazole and benzyl bromide with potassium carbonate for 72 h (Reid, 1996). Crystals were obtained from methanol.

Crystal data

$C_{14}H_{11}N_3O_2$
M_r = 253.26
Orthorhombic, $P2_12_12_1$
a = 12.2039 (8) Å
b = 12.2039 (8) Å
c = 8.3430 (10) Å
V = 1242.57 (19) Å^3
Z = 4
D_x = 1.354 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 19.0–21.0°
μ = 0.09 mm^{-1}
T = 298 (2) K
Prism, colourless
0.35 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
1277 measured reflections
1277 independent reflections
655 reflections with $I > 2\sigma(I)$
θ_{max} = 25.0°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: 10.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.102
S = 1.00
1277 reflections
176 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.019 (3)
Absolute structure: Flack (1983)

Although the a and *b* cell parameters were identical, no symmetry higher than orthorhombic could be identified. The positional parameters of only the carboxylic acid H atom were refined: the remaining H atoms were included in the model in their geometrically calculated positions and included in the final refinement in the riding-model approximation.

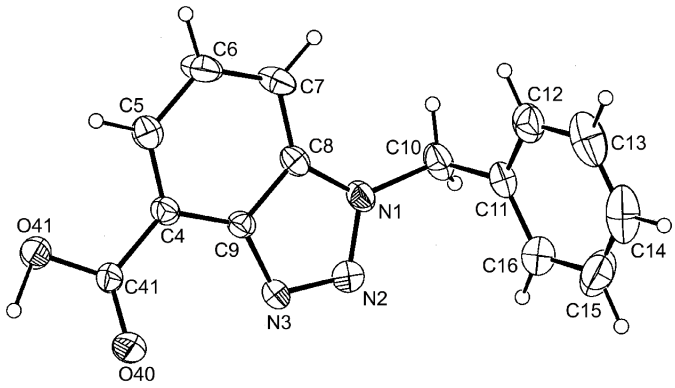


Figure 1
The molecular configuration and atom-numbering scheme for (I). Atoms are shown as 30% probability ellipsoids (Johnson, 1976).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON* (Spek, 1999).

The authors acknowledge financial support from The Centre for Instrumental and Developmental Chemistry (Queensland University of Technology), and the Australian Research Council.

References

Cotton, J. B. (1963). *Proceedings of the International Congress on Metal Corrosion*, pp. 590–592. New York: NACE.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Frignani, A., Fonsati, M., Monticelli, C. & Brunoro, G. (1999). *Corros. Sci.* **41**, 1217–1227.
Huynh, N., Notoya, T., Bottle, S. E. & Schweinsberg, D. P. (2000). *Corros. Sci.* **42**, 259–272.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mansfeld, F., Smith, T. & Parry, E. P. (1971). *Corrosion*, **27**, 289–294.
Molecular Structure Corporation (1999*a*). *MSC/AFC Diffractometer Control Software*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1999*b*). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Otieno-Alego, V., Huynh, N., Notoya, T., Bottle, S. E. & Schweinsberg, D. P. (1999). *Corros. Sci.* **41**, 685–697.
Reid, D. A. (1996). BSc (Hons) Thesis, Queensland University of Technology, Brisbane, Australia.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1999). *PLATON*. September 1999 version. University of Utrecht, The Netherlands.
Wu, J. S. & Nobe, K. (1981). *Corrosion*, **37**, 223–225.
Xue, G., Ding, J., Lu, P. & Dong, J. (1991). *J. Phys. Chem.* **95**, 7380–7385.