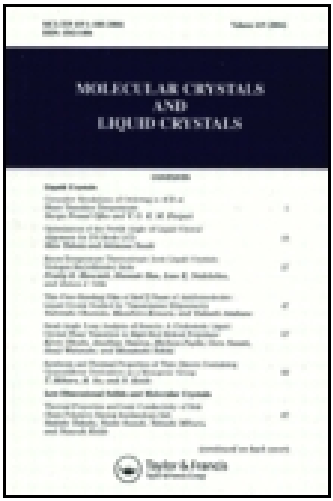


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

ROLE OF WEAK INTERACTIONS IN THE STRUCTURE OF 3-(α,α′-DIBROMOMETHYL)BENZYL 1-4 BENZOTRIAZOLE (DBT)

S. M. Malathy Sony [a], M. Kuppayee [a], M. N. Ponnuswamy [a], V. Murali [b] & P. Rajakumar [b]

[a] Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai-600 025, India

[b] Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai-600 025, India

Published online: 02 Feb 2011.

To cite this article: S. M. Malathy Sony , M. Kuppayee , M. N. Ponnuswamy , V. Murali & P. Rajakumar (2003) ROLE OF WEAK INTERACTIONS IN THE STRUCTURE OF 3-(α,α′-DIBROMOMETHYL)BENZYL 1-4 BENZOTRIAZOLE (DBT), Molecular Crystals and Liquid Crystals, 403:1, 15-22, DOI: 10.1080/744818942

To link to this article: http://dx.doi.org/10.1080/744818942

Mol. Cryst. Liq. Cryst., Vol. 403, pp. 15–22, 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390234020

Taylor & Francis
Taylor & Francis Group

ROLE OF WEAK INTERACTIONS IN THE STRUCTURE OF 3-(α,α′-DIBROMOMETHYL)BENZYL 1-4 BENZOTRIAZOLE (DBT)†

*S. M. Malathy Sony, M. Kuppayee, and M. N. Ponnuswamy**
Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai-600 025, India

V. Murali and P. Rajakumar
Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai-600 025, India

3-(α,α′-Dibromomethyl)benzyl 1-4 benzotriazole, $C_{14}H_{11}Br_2N_3$, F.W. = 381.08, triclinic, $P\bar{1}$, a = 8.411(1)Å, b = 9.008(1)Å, c = 9.714(1)Å, α = 97.74(1)°, β = 103.11(1)°, γ = 101.62(1)°, V = 689.4(1)Å^3, Z = 2, $D_{cal} = 1.836\,Mgm^{-3}$, $\mu = 7.364\,mm^{-1}$, λ(CuKα) = 1.5418Å, final R1 and wR2 are 0.0538 and 0.1383, respectively.

The title compound is a precursor for the macroligand stilbenobenzotriazolophane. Unusual short bond length in the benzotriazole ring suggests the delocalization effect on the bonding. Intermolecular C-H . . . π, C-H . . . Br, *and some face-to-face π-π interactions play a role in stabilizing the delocalized form. The molecules in the unit cell are stabilized by* C-H . . . N *type of interactions in addition to van der Waals forces.*

Keywords: π-interactions; benzotriazole; delocalization; crystal structure; hydrogen bond

INTRODUCTION

Triazoles are synthetic intermediates derived from hydrazine hydrate. Amino 1,2,4-triazoles are used for the synthesis of active ingredients for phytosanitary, pharmaceutical, and veterinary products and photographic products.

Benzotriazole and its derivatives comprise an important class of corrosion inhibitors, typically used as trace additives in industrial chemical

Received 3 December 2002; accepted 5 May 2003.
†The CDB Reference Number: DBT - CCDC 200294.
*Corresponding author. E-Mail: mnpsy@hotmail.com

mixtures such as coolants, deicers, surface coatings, cutting fluids, and hydraulic fluids. Recent studies have shown that benzotriazole derivatives are a major component of aircraft deicing fluids (ADFs) responsible for toxicity to bacteria [1].

1H-benzotriazole derivatives containing thiazolin, thiazolidin, thiadiazole, and oxadiazole moieties showed anti-inflammatory activity and also demonstrate minimum ulcerogenic activity [2]. Hydroxybenzoyl-benzotriazoles activated potassium channels showed vasorelaxing properties [3]. Amino-benzotriazole is an inhibitor of Cytochrome P-450 (Cyt P-450) [4] and some piperazinyl-benzotriazoles bind to the serotonin 5-HT1A receptor and exhibit good analgesic, antihypertensive activity and adrenergic α_1 antagonism [5]. Hydroazepin-3-yl-benzotriazole-5-carboxamides derivatives showed potent antiemetic activity and gastroprokinetic activity [6].

The benzotriazole under study is a precursor for the macroligand stilbenobenzotriazolophane whose structural study will provide an idea for the chemists to obtain the required final product.

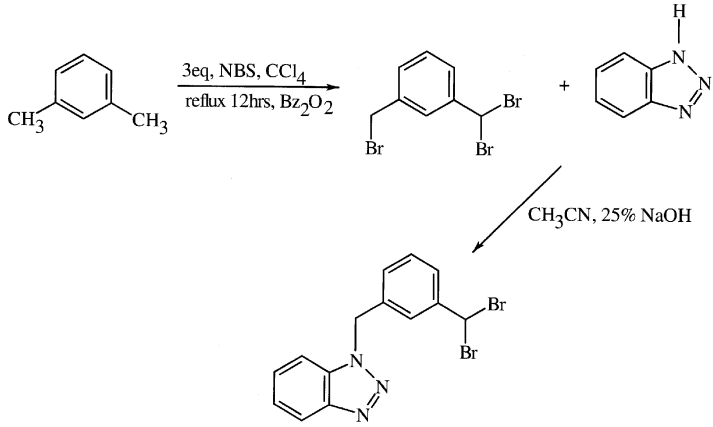
EXPERIMENTAL

Preparation of the Compound

m-Xylene was added to three equivalent moles of N-bromo succinimide in CCl_4. This mixture was refluxed for 12 h, and periodically benzyl peroxide was added, which was then cooled. The precipitate of tribromide was purified and reacted with benzotriazole in the presence of 25% of sodium hydroxide and methyl cyanide at room temperature for 2 days. The crude product was extracted with methylene chloride. The organic layer was dried and recrystallized from methylene chloride/hexane (Scheme I).

X-ray Data Collection, Structure Solution and Refinement

Transparent rectangular plate-shaped crystal of dimension $0.25 \times 0.30 \times 0.15$ mm was chosen for the intensity data collection on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated CuKα ($\lambda = 1.5418$ Å) radiation [7]. Accurate unit cell parameters were obtained from 25 reflections in the range $15 \leq \theta \leq 25^\circ$ from least-squares refinement. The intensities were measured to a maximum 2θ of 144.68° by $\omega/2\theta$ scan mode. Three standard reflections monitored for every hundred reflections for intensity check showed little or no decay ($< 1\%$) throughout the data collection. Out of 2553 ($R_{int} = 0.0493$) independent reflections collected, 2383 reflections with $I \geq 2\sigma(I)$ were used for structure analysis. The intensities were corrected for Lorentz and polarization effects using



SCHEME 1 Synthetic pathway of the title compound.

TABLE 1 Crystal Data

Parameter	DBT
Empirical formula	$C_{14}H_{11}Br_2N_3$
Formula weight	381.08
Wavelength (Å)	1.54178
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a(Å)	8.411(1)
b(Å)	9.008(1)
c(Å)	9.714(1)
α(°)	97.74(1)
β(°)	103.11(1)
γ(°)	101.61(1)
Volume (Å^3)	689.43(13)
Z, Calculated density(Mg/m^3)	2, 1.836
Absorption coefficient(mm^{-1})	7.364
F(000)	372
Theta range for data collection(°)	4.76 to 72.34
Index ranges	$-10 \leq h \leq 10$ $0 \leq k \leq 8$ $-11 \leq l \leq 11$
Reflections collected/unique	2553/2383 [R(int) = 0.0493]
Completeness to $\theta = 72.34$	87.3%
Data/restraints/parameters	2383/0/173
Goodness-of-fit on F^2	1.071
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0538, wR2 = 0.1383
R indices (all data)	R1 = 0.0706, wR2 = 0.1702
Extinction coefficient	0.0250(17)
Largest diff. peak and hole (e. Å^{-3})	0.742 and −0.980

the data reduction program XCAD4PC [8]. Cylindrical-type absorption correction was carried using C. W. Dwiggins Jr.'s [9] method, and the minimum and maximum transmission values (T_{min} and T_{max}) are 0.1971 and 0.2847, respectively.

The structure was solved by direct methods using the program SHELXS97 [10]. The structure was refined on F^2 by full-matrix least-squares procedures using the program SHELXL97 [11]. The nonhydrogen atoms were refined anisotropically, and all the hydrogens were fixed as riding model over their heavier atoms. The final cycle of refinement converged to $R_1 = 0.0538$ and $wR_1 = 0.1383$ for the observed reflections. The maximum and minimum heights in the final difference Fourier map were found to be 0.742 and $-0.980 e/Å^3$, respectively. The geometrical calculations and the figures were done by using the programs PLATON [12] and ZORTEP [13], respectively.

RESULTS AND DISCUSSION

The crystal data and the other relevant parameters are given in Table 1. The atomic coordinates with their equivalent isotropic displacement factors for nonhydrogen atoms are presented in Table 2 and the perspective view of the molecule is shown in Figure 1.

The bond lengths and bond angles are comparable with the values reported in the literature [14], except for the bond C12-C13 [1.296(9) Å], which possesses more of a double bond character. This may be due to the delocalization of electrons in the bonding [15], which is attributed by some weak intermolecular interactions made by the benzotriazole ring (Figure 2). The benzotriazole ring makes face-to-face π-π intermolecular interaction with the symmetry-related benzotriazole ring $(2-x, -y, -z)$ with centroid-centroid distance of 4.0882Å and the dihedral angle between the planes, $\alpha = 0.00°$. The benzyl ring also interacts face to face with its symmetry-related $(2-x, 1-y, 1-z)$ molecule with $Cg - Cg = 3.6647Å$ (Cg → centroid of the π-system) and $\alpha = 0.03°$ [16–18]. In addition to these interactions, the molecule also has C-H…π intermolecular interactions where the benzyl π-system (Cg2) interacts with C13 & C14 atoms (Table 3). Analysis of the short intermolecular contacts implied that the bromine atom Br2 makes a weak bifurcated C-H…Br interaction with C12 [x, 1 + y, 1 + z] and C15 [x, 1 + y, z] atoms (H12…Br2 = 3.042 Å and H15…Br2 = 3.037Å) (Figure 3) [18]. All these weak interactions help in stabilizing the delocalized form.

The benzotriazole ring is planar and oriented to the benzyl ring at an angle of 83.7(2)°. This geometry also creates a favorable edge-to-face π-π intramolecular interaction between these rings with the Cg – Cg distance

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) Involving Nonhydrogen Atoms

Atom	*x*	*y*	*z*	*U(eq)
Br1	4184(1)	5648(1)	1658(1)	71(1)
Br2	7234(1)	8303(1)	3658(1)	79(1)
C1	8949(7)	3240(8)	2977(7)	48(2)
C2	8283(7)	4337(7)	2378(6)	41(1)
C3	7335(7)	5131(7)	3061(6)	39(1)
C4	7055(8)	4812(8)	4358(7)	51(2)
C5	7762(9)	3707(9)	4975(8)	56(2)
C6	8687(9)	2929(8)	4278(8)	57(2)
C7	10089(9)	2447(10)	2307(9)	68(2)
N8	9603(6)	2136(6)	769(7)	52(1)
N9	10388(8)	3053(7)	−11(9)	71(2)
N10	9720(10)	2560(8)	−1346(10)	79(2)
C11	8537(9)	1313(8)	−1515(8)	54(2)
C12	7297(13)	348(11)	−2741(10)	78(2)
C13	6184(12)	−801(12)	−2591(12)	83(3)
C14	6098(10)	−1109(10)	−1240(15)	89(3)
C15	7159(9)	−209(9)	7(10)	66(2)
C16	8340(7)	1017(7)	−163(8)	47(2)
C17	6629(8)	6306(7)	2367(7)	47(2)

*U(eq) = (1/3) $\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a_i}.\mathbf{a_j}$.

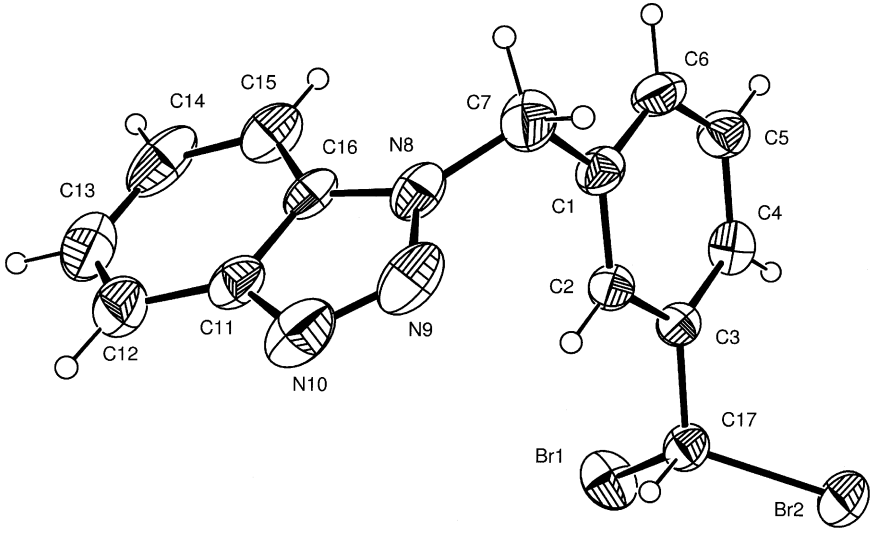


FIGURE 1 ZORTEP plot of the molecule with 30% probability displacement ellipsoids and with atomic numbering scheme.

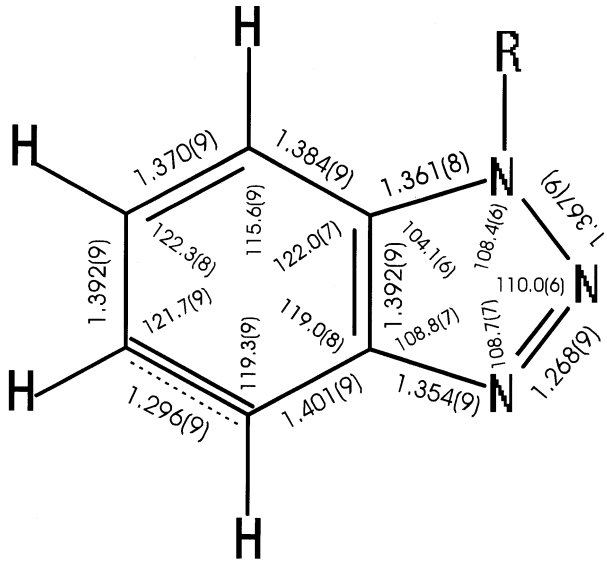


FIGURE 2 Possible delocalized form of the benzotriazole ring in the molecule.

of 4.6150 Å ($\alpha = 83.73°$) and 5.4738 Å ($\alpha = 83.37°$) from the triazole and the benzene ring of benzotriazole ring to the benzyl ring, respectively. The benzyl ring is planar and the maximum deviation observed for the atoms is

TABLE 3 Possible Nonbonded Interactions

d(D-H)Å	d(D . . . A)Å	d(H . . . A)Å	<(DHA)°
C2-H2	C2 . . . N9	H2 . . . N9	C2-H2 . . . N9 (1)
0.93	3.44(1)	2.838	123.4(4)
C2-H2	C2 . . . N9	H2 . . . N9	C2-H2 . . . N9 (2)
0.93	3.69(1)	2.888	145.4(4)
C2-H2	C2 . . . N10	H2 . . . N10	C2-H2 . . . N10 (2)
0.93	3.36(1)	2.782	121.0(4)
C17-H17	C17 . . . N9	H17 . . . N9	C17-H17 . . . N9 (2)
0.98	3.77(1)	2.851	157.3(4)
C17-H17	C17 . . . N10	H17 . . . N10	C17-H17 . . . N10 (2)
0.98	3.44(1)	2.709	131.9(4)
C13-H13	C13 . . . Cg2	H13 . . . Cg2	C13-H13 . . . Cg2 (3)
0.93	3.920	3.260	129.5
C14-H14	C14 . . . Cg2	H14 . . . Cg2	C14-H14 . . . Cg2 (3)
0.93	3.926	3.270	128.9

Equivalent positions: (1) x+1,+y,+z; (2) −x+1,−y+1,−z; (3) 1−x,−y,−z. Cg2, Centroid of the benzyl ring.

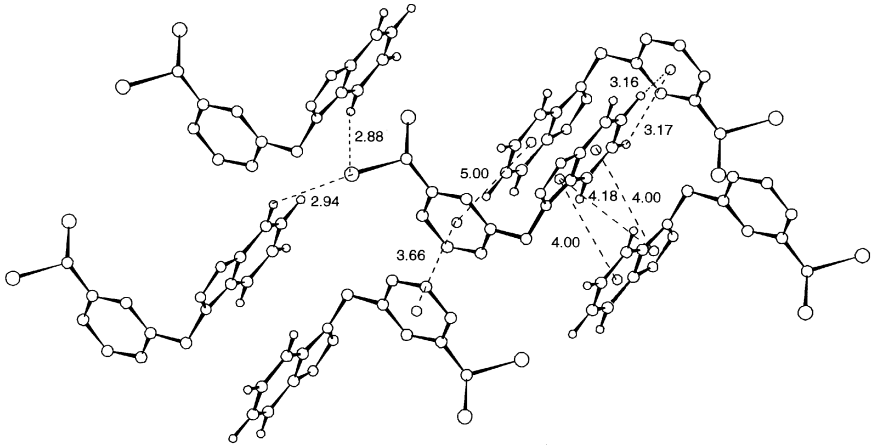


FIGURE 3 Diagram illustrating all possible interactions of the molecule.

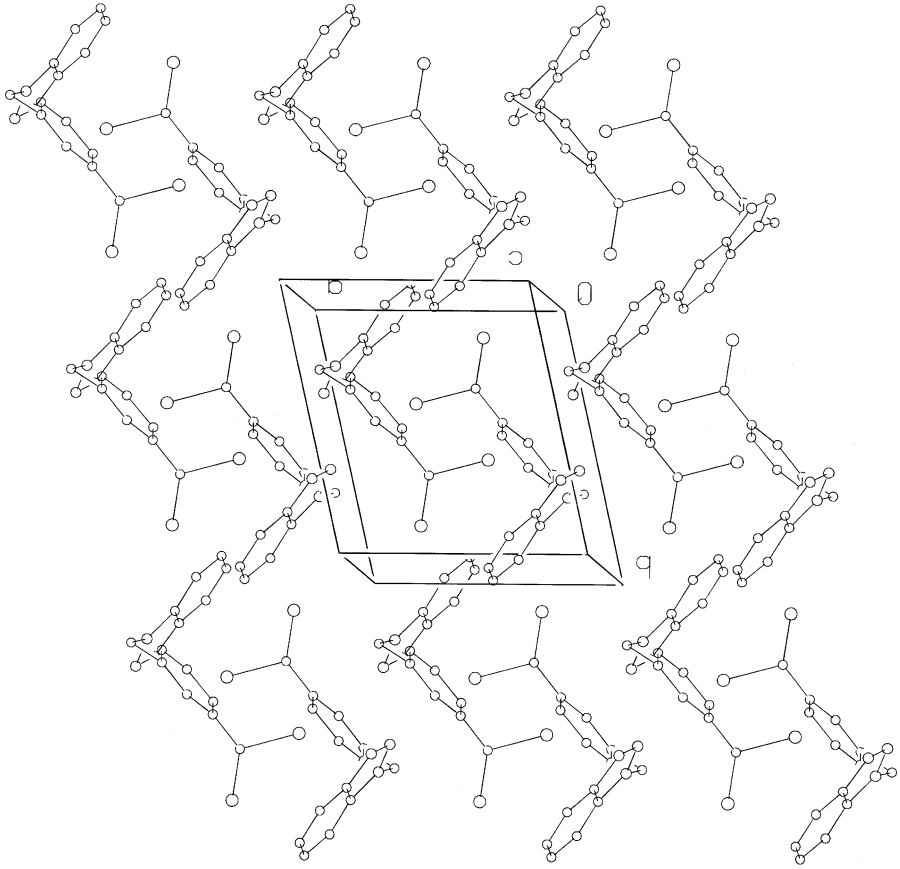


FIGURE 4 Packing of the molecules viewed down *c* axis.

0.008(8) Å for C5. The packing of the molecules viewed down the c-axis is shown in Figure 4. The bifurcated C-H . . . Br intermolecular interaction forms an interaction network along the z-direction and the C17-H17 . . . N10 hydrogen bond forms a network along *y* direction. These two intermolecular networks arrange the molecules in a two-dimensional linear polymer fashion in the crystal lattice. The molecules in the crystal are stabilized by C-H . . . N type of intermolecular interactions, in addition to van der Waals forces (Table 3).

REFERENCES

[1] Pillard, D. A., Cornell, J. S., Dufresne, D. L., & Hernandez, M. T. (2001). *Water Res.*, *35*(2), 557.
[2] Habib, N. S., Fahmy, S., El-Khawass, S. M., & Abel Aziem, T. A. (2000). *Pharmazie.*, *55*(12), 900.
[3] Biagi, G., Giorgi, I., Livi, O., Scartoni, V., Barili, P. L., Calderone, V., & Martinotti, E. (2001). *Farmaco.*, *56*(11), 827.
[4] Ceresa. F., Delfino, A., De Matteis, A., Ferrero, N., Novarino, M., & Ritta, A. (1999). *Boll. Soc. Ital. Biol. Sper.*, *75*(1–2), 1.
[5] Boido, A., Boido, C. C., & Sparatore, F. (2001). *Farmaco.*, *56*(4), 263.
[6] Hirokawa, Y., Yamazaki, H., Yoshida, N., & Kato, S. (1998). *Bioorg. Med. Chem. Lett.*, *8*(15), 1973.
[7] Enraf-Nonius. (1994). *CAD-4 Express Software*. Delft, The Netherlands: Enraf-Nonius.
[8] Harms, K., & Wocaldo, S. (1995). *XCAD4PC. Programs for processing CAD-4 Diffractometer Data*. Marburg, Germany: University of Marburg.
[9] Dwiggins, C. W., Jr., (1975). *Acta Cryst.*, *A31*, 146.
[10] Sheldrick, G. M. (1997). *SHELXS97. Program for the Crystal Structure Solution*. Göttingen, Germany: University of Göttingen.
[11] Sheldrick, G. M. (1997). *SHELXL97. Program for the Crystal Structure Refinement*. Göttingen, Germany: University of Göttingen.
[12] Spek, A. L. (1998). *PLATON. A Multipurpose Crystallographic Tool*, Utrecht, The Netherlands: Utrecht University.
[13] Zsolani, L. (1997). *ZORTEP. Program for Crystal Structure Illustration*, Heidelberg, Germany: University of Heidelberg.
[14] Allen, F. H., Kennard, O., Watson, D. G., Brummer, L., Orpen, A. G., & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.*, *II*, S1.
[15] Fayos, J., & Garcia-Blanco, S. (1972). *Acta Cryst.*, *B28*, 2863.
[16] Jorgensen, W. L., & Severance, D. L. (1990). *J. Am. Chem. Soc.*, *112*, 4768.
[17] Hunter, C. A., & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.*, *112*, 5525.
[18] Desiraju, G. R. (1989). *Material Science Monographs, 54, Crystal Engineering. The Design of Organic Solids*, New York: Elsevier Science Publishers.