Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

tert-Butyl *N*-(2-bromocyclohex-2-enyl)-*N*-(2-furylmethyl)carbamate

Başak Koşar,[a] Aydın Demircan,[b] Muhsin Karaarslan[b] and Orhan Büyükgüngör[a]*

[a]Department of Physics, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, and [b]Department of Chemistry, Nigde University, TR-51100 Nigde, Turkey

Correspondence e-mail: bkosar@omu.edu.tr

Received 14 December 2005
Accepted 18 January 2006

Key indicators

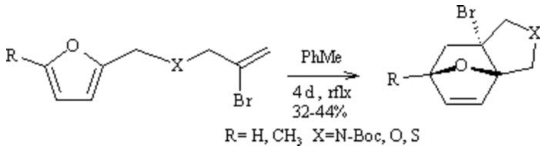
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.014 Å
R factor = 0.071
wR factor = 0.179
Data-to-parameter ratio = 17.4

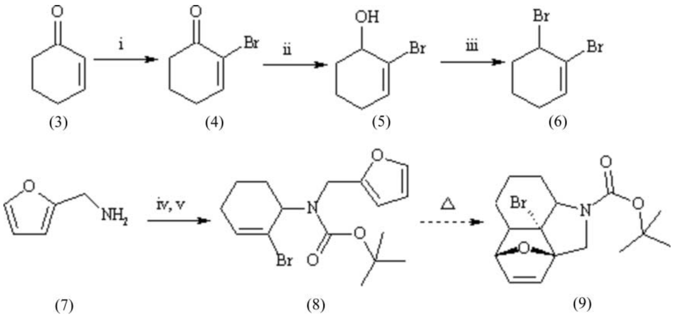
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{16}H_{22}BrNO_3$, the molecules are linked only by weak van der Waals interactions. The bromo attached cyclohexane ring adopts a half-chair conformation.

Comment

The intramolecular Diels–Alder (IMDA) reaction is a widely utilized synthetic strategy for the simultaneous formation of two rings with high regio- and stereocontrol (Lipshutz, 1986). The use of a furan component in the IMDA reaction leads to the creation of an oxygenated cyclohexene ring in a rigid cycloadduct that has potential application for the synthesis of natural products such as carbohydrates and prostaglandins (Bear *et al.*, 2001). However, the facile retro-Diels–Alder reaction and the low reactivity of furan as a diene, as a result of its aromatic character, make the Diels–Alder reaction of furan one of the most difficult cycloadditions (Kappe *et al.*, 1997). Additionally, heteroatoms attached to furans have been found to be internal chiral auxiliaries, or to result in ring formation for natural product synthesis (Andres *et al.*, 2002). We have extensively studied the IMDA reaction of the furan diene (IMDAF) when the linkage connecting the diene and the dienophile consists of three atoms and contains a heteroatom (Demircan & Parsons, 1998, 2002; Büyükgüngör *et al.*, 2005). In this paper, we present an X-ray crystallographic analysis of the title compound, (8).





The scheme shows the reaction between di-tert-butoxy dicarbonate [$(Boc)_2O$], dimethylaminopyridine (DMAP) and dichloromethane. We now report our findings on the IMDAF aspect; the synthesis and crystal-structure determination of

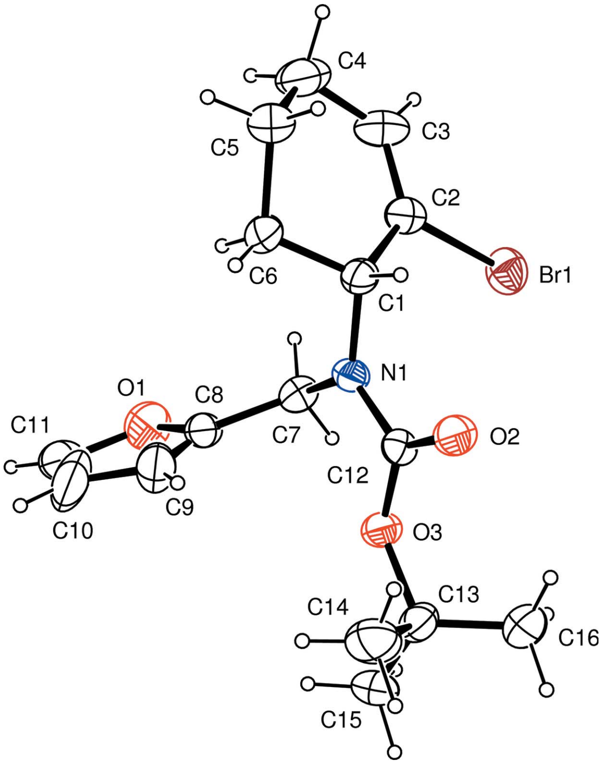


Figure 1
A view of compound (8), with the atom-numbering scheme and 50% probability displacement ellipsoids.

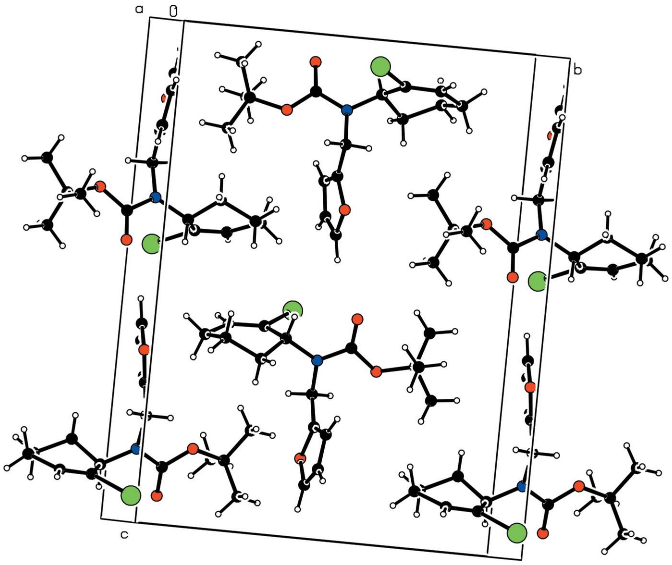


Figure 2
A packing diagram of compound (8).

the title compound have been achieved, and this compound is a precursor of the tetracycle (9). The synthesis of compound (9) was accomplished in several high-yield steps from cyclohexenone (3) using the process shown in the scheme. Addition of bromine and triethylamine to (3) was followed by selective Luche reduction of (4) with sodium borohydride in the presence of cerium chloride heptahydrate to afford the bromoalcohol (5). Substitution of (5) with phosphorus tribromide gave 2,3-dibromocyclohexene (6) in 68% yield. In the scheme the steps are as follows: (i) Br_2, Et_3N, dichloromethane, 273 K, 98%; (ii) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH, 273 K, 97%; (iii) PBr_3, pyridine, PhH, 273 K → reflux, 68%; (iv) 2,3-dibromocyclohexene (6), K_2CO_3, tetrahydrofuran, reflux, 3 d, 93%; (v) $(Boc)_2O$, DMAP, dichloromethane, 273 K, 2 h, 80%.

Conversion of (6) to the amine (8) was realised by two high-yield steps. Commercially available furfurylamine (7) was added to 2,3-dibromocyclohexene with potassium carbonate in tetrahydrofuran; protection of the resulting secondary amine with di-*tert*-butoxy dicarbonate was generated under standard conditions and gave the desired compound, (8), in 80% yield.

The molecular structure of (8) is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. Fig. 2 shows the packing of the molecules in the unit cell. The bromo-substituted cyclohexene ring adopts a half-chair conformation, with torsion angles as given in Table 1. Atom C9 deviates from the C8–C11/O1 ring plane by 0.015 (9) Å. The Br—C bond distance [1.939 (9) Å] is not significantly different from the value reported for a pure Br—C single bond (1.94 Å; Toprak *et al.*, 2001).

Experimental

2-Bromo-*N*-(furan-2-ylmethyl)cyclohex-2-enamine, (1), was synthesized as follows. To a stirred solution of furfurylamine (7) (1.13 g, 11.66 mmol) in tetrahydrofuran (40 ml) was added 2,3-dibromocyclohexene (1.40 g, 5.83 mmol) and the resulting solution was heated to reflux for 12 h. A portion of potassium carbonate (3.70 g, 26.02 mmol) was then added, and the reaction mixture was heated at reflux for a further 48 h. On cooling, a precipitate was formed which was washed with diethyl ether (3 × 25 ml). The filtrate was extracted with 10% NaOH (40 ml) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was used in the next reaction without further purification (1.37 g, 93%).

tert-Butyl *N*-(2-bromocyclohex-2-enyl)-*N*-(2-furylmethyl)carbamate, (8), was synthesized as follows. To a stirred solution of 2-bromo-*N*-(furan-2-ylmethyl)cyclohex-2-enamine, (1) (1.37 g, 5.35 mmol), and di-*tert*-butoxy dicarbonate, $(Boc)_2O$ (1.17 g, 5.35 mmol) in dichloromethane (10 ml) was added *N*,*N*-dimethylaminopyridine (0.07 g, 0.54 mmol) at 273 K. The reaction mixture was stirred for 2 h at ambient temperature and then concentrated under a vacuum. The residue was subjected to flash column chromatography to afford the title compound, (8), as colourless crystals (1.52 g, 80%). Thin-layer chromatography [hexane–ethyl acetate (4:1)]: R_f 0.75; IR (ν_{max}, thin film, cm^{-1}): 2975 (*s*, C—H), 2933 (*s*, C—H), 1702 (*s*, C=O), 1164 (*s*, C—O), 607 (*m*, C—Br); ^1H NMR (200 MHz, $CDCl_3$, δ, p.p.m.): 7.32 (*d*, 1H, J = 1.9 Hz), 6.34–6.30 (*m*, 1H), 6.24 (*dd*, 1H, J_1 = 1.9 Hz, J_2 = 3.1 Hz, AB), 6.14 (*d*, 1H, J = 3.1 Hz), 4.92–4.90 (*m*, 1H), 4.51 (*d*, 1H, J_1 = 16.4 Hz, AB), 3.92 (*d*, 1H, J_2 = 16.4 Hz, AB), 2.13–1.58 (*m*, 6H), 1.43 (*s*, 9H); ^{13}C NMR (50 MHz, $CDCl_3$, δ, p.p.m.): 155.3 (*q*), 153.7 (*q*), 143.4, 133.5, 127.3 (*q*), 113.4, 109.1, 82.2 (*q*), 58.0, 45.1, 29.7, 29.0 (3C), 28.4, 21.5; GC–MS, *m*/*z*: 357 $[M^+(^{81}Br)$, 10%], 355 $[M^+(^{79}Br)$, 10%], 300 $[M^+(^{81}Br) - (^tBu)$, 15%], 298 $[M^+(^{79}Br) - (^tBu)$ 15%], 256 $[M^+(^{81}Br) - (Boc)$ 100%], 254 $[M^+(^{79}Br) - (Boc)$ 100%], 161, 81, 57; elemental analysis: calculated (found): C 53.94 (53.61), H 6.22 (6.51), N 393 (3.70)%.

o766 Koşar et al. • $C_{16}H_{22}BrNO_3$ Acta Cryst. (2006). E62, o765–o767

Crystal data

$C_{16}H_{22}BrNO_3$
$M_r = 356.26$
Orthorhombic, $P2_12_12_1$
$a = 6.2089$ (4) Å
$b = 14.6385$ (13) Å
$c = 18.5957$ (12) Å
$V = 1690.1$ (2) Å^3
$Z = 4$
$D_x = 1.400$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4938 reflections
$\theta = 1.8$–28.1°
$\mu = 2.44$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.61 × 0.45 × 0.20 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
$T_{\min} = 0.218$, $T_{\max} = 0.567$
16581 measured reflections
3327 independent reflections
2788 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 26.0°$
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.071$
$wR(F^2) = 0.180$
$S = 1.13$
3327 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 6.2411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}
Absolute structure: Flack (1983), with 1389 Freidel pairs
Flack parameter: 0.49 (3)

Table 1
Selected geometric parameters (Å, °).

C2—Br1	1.939 (9)	C12—O2	1.189 (8)
C8—O1	1.385 (12)	C12—O3	1.328 (7)
C11—O1	1.412 (18)	C13—O3	1.463 (9)
C1—C2—C3—C4	−1.2 (16)	C3—C4—C5—C6	−44.8 (13)
C2—C3—C4—C5	14.8 (16)		

All H atoms were treated using a riding model, with C—H = 0.96–0.98 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The value of the Flack parameter (Flack, 1983) indicates an inversion twin.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank TUBITAK for financial support of this work [project No. 2377(103 T121)], and Professor Dr Hasan Seçen for his interest.

References

Andres, C., Maestro, G., Nieto, J., Pedrosa, R., Gracia-Granda, S. & Perez-Carreno, E. (1997). *Tetrahedron Lett.* **38**, 1463–1466.
Bear, B. S., Sparks, S. M. & Shea, K. (2001). *Angew. Chem. Int. Ed.* **40**, 820–849.
Büyükgüngör, O., Koşar, B., Demircan, A. & Turaç, E. (2005). *Acta Cryst.* E**61**, o1441–1442.
Demircan, A. & Parsons, P. J. (1998). *Synlett*, pp. 1215–1216.
Demircan, A. & Parsons, P. J. (2002). *Heterocycl. Commun.* **8**, 531–536.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kappe, C. O., Murphree, S. S. & Padwa, A. (1997). *Tetrahedron*, **53**, 14179–14233.
Lipshutz, B. H. (1986). *Chem. Rev.* **86**, 795–819.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
Toprak, M., Alp, S. & Karagöz, S. (2001). *Organic Chemistry*. Dokuz Eylül University Press.

Acta Cryst. (2006). E**62**, o765–o767 Koşar *et al.* • $C_{16}H_{22}BrNO_3$ **o767**