

5,5a-Diallyl-5,5a,13,14-tetrahydro-12H-di-1,3-benzimidazolo[1,2-a;1',2'-c][1,4]diazepine

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Key indicators

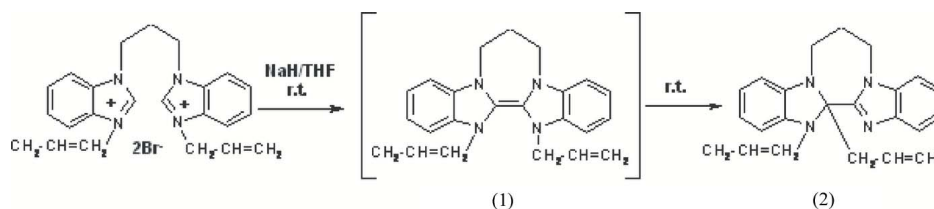
Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(C-C) = 0.003$ Å
 R factor = 0.033
 wR factor = 0.089
Data-to-parameter ratio = 10.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, $C_{23}H_{24}N_4$, was synthesized from 3,3'-diallyl-1,1'-propylendi(benzimidazole) dibromide and NaH in tetrahydrofuran solution. In the molecule, the diazepine ring exhibits a boat conformation.

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Comment

Electron-rich olefins have attracted considerable attention in both the organic and inorganic preparative literature as a result of their unique properties as reagents and reaction intermediates (Böhm & Herrmann, 2000). They have been used as powerful reducing agents (Lappert, 1988), sources of carbene transition metal complexes (Küçükbay *et al.*, 1996) and catalysts for acyloin type C–C coupling reactions (Çetinkaya & Küçükbay, 1995). They have an extensive chemistry and, in particular, electron-rich olefins that contain an imidazolidine or benzothiazolidine group have long been known, although there are few studies of electron-rich olefins containing a benzimidazolidine group. Isolation of allyl-, crotyl- or benzyl-substituted electron-rich olefins tends to be difficult because the synthesized olefins spontaneously transform to their [1,3]-sigmatropic rearrangement products. As was previously reported (Baldwin & Walker, 1974; Baldwin *et al.*, 1977; Çetinkaya *et al.*, 1998), we also obtained a [1,3]-sigmatropic rearrangement product, namely 2',3'-diallyl-2',3'-*H*-dibenzimidazolo[a,c]perhydro-1,4-diazepine, (2), instead of the corresponding electron-rich olefin, (1), from a reaction of 3,3'-bis(allyl)-1,1'-propylendi(benzimidazole) dibromide and NaH in THF solution. The crystal structure of (2) is presented here.



The molecular structure of (2) is shown in Fig. 1. The geometric parameters in (2) are within the normal ranges (Allen *et al.*, 1987) and agree with those in similar structures reported in the literature (Mague & Eduok, 2000; Akkurt *et al.*, 2006a,b). The diazepine ring exhibits a boat conformation. The displacements of atoms N3, C17 and C8 from the C1/N2/C9/C10 mean plane are 0.398 (1), 0.214 (2) and 0.562 (2) Å, respectively. The benzimidazole ring systems in (2) are essentially planar and the dihedral angle between them is 75.56 (5)°.

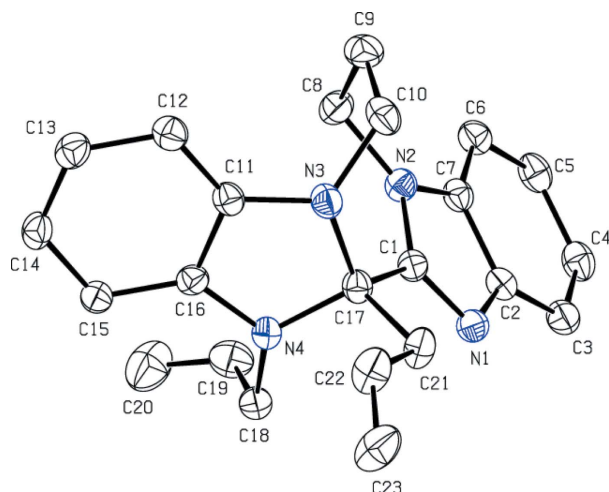


Figure 1
Molecular structure of (2), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms have been omitted.

The molecular conformation of (2) is stabilized by an intramolecular C—H···N hydrogen-bonding interaction (Table 2).

Experimental

A mixture of 3,3'-bis(allyl)-1,1'-propylendi(benzimidazole) dibromide (5.0 g, 9.7 mmol) and NaH (0.5 g, 21 mmol) in THF (50 ml) was stirred for 10 h at room temperature. Volatiles were eliminated *in vacuo*, toluene (20 ml) was added and the suspension was filtered. The resulting bright-yellow filtrate was concentrated to ca 10 ml and *n*-hexane (10 ml) was added. Upon cooling, colourless crystals of (2) (2 g, 53%) were obtained (m.p. 408–409 K). ¹H NMR (CDCl₃): δ 1.6–1.8 (*m*, —CH₂—bridge, 2H), 3.0–3.2 (*d*, —CH₂—, 2H), 3.7–4.0 (*m*, —N—CH₂—bridge, 4H), 4.2 (*d*, N—CH₂—, 2H), 4.8–5.0 (*q*, =CH₂, 2H), 5.1–5.3 (*q*, =CH₂, 2H), 5.4–5.6 (*m*, —CH=, 1H), 5.9–6.1 (*m*, —CH=, 1H), 6.2–7.8 (*m*, Ar—H, 8H). Analysis calculated for C₂₃H₂₄N₄: C 77.53, H 6.74, N 15.73%; found: C 76.62, H 6.98, N 16.40%.

Crystal data

C ₂₃ H ₂₄ N ₄	Z = 4
<i>M_r</i> = 356.46	<i>D_x</i> = 1.276 Mg m ⁻³
Orthorhombic, <i>Pca</i> 2 ₁	Mo Kα radiation
<i>a</i> = 25.1810 (13) Å	<i>μ</i> = 0.08 mm ⁻¹
<i>b</i> = 8.304 (5) Å	<i>T</i> = 150 (2) K
<i>c</i> = 8.878 (8) Å	Irregular, colourless
<i>V</i> = 1856 (2) Å ³	0.44 × 0.43 × 0.39 mm

Data collection

Bruker SMART CCD area-detector diffractometer	18216 measured reflections
<i>φ</i> and <i>ω</i> scans	2499 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	2334 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.967, <i>T_{max}</i> = 0.970	<i>R_{int}</i> = 0.030
	<i>θ_{max}</i> = 28.6°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.033
wR (*F*²) = 0.089
S = 1.02
 2499 reflections
 244 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.4382P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C22—H22···N3	0.93	2.56	2.912 (4)	103

H atoms were placed in geometrically idealized positions and constrained to ride on their parents atoms, with C—H = 0.93–0.97 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C). In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *APEXII* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); 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).

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