C(20)	0.4609 (5)	0.1995 (9)	0.4091 (4)	0.061 (2)
C(21)	0.6112 (4)	0.3210 (8)	−0.0298 (3)	0.045 (2)
C(22)	0.5101 (4)	0.2963 (9)	−0.1206 (4)	0.055 (2)
C(23)	0.5286 (5)	0.3163 (10)	−0.2356 (4)	0.067 (2)
C(24)	0.6467 (5)	0.3628 (10)	−0.2603 (4)	0.064 (2)
C(25)	0.7453 (5)	0.3912 (10)	−0.1722 (4)	0.071 (2)
C(26)	0.7278 (5)	0.3707 (10)	−0.0571 (4)	0.064 (2)

Table 2. *Selected geometric parameters (Å, °)*

O(3)—C(6)	1.386 (5)	C(22)—C(21)	1.388 (6)
O(3)—C(2)	1.378 (6)	C(22)—C(23)	1.384 (7)
C(5)—C(4)	1.522 (6)	C(14)—C(13)	1.383 (7)
C(5)—C(6)	1.328 (6)	C(14)—C(15)	1.379 (7)
C(5)—C(20)	1.461 (7)	C(18)—C(13)	1.392 (6)
C(3)—C(4)	1.509 (6)	C(18)—C(17)	1.384 (7)
C(3)—C(2)	1.339 (7)	O(1)—C(19)	1.203 (7)
C(3)—C(19)	1.447 (8)	C(17)—C(16)	1.365 (9)
C(7)—C(4)	1.523 (8)	C(8)—C(9)	1.377 (10)
C(7)—C(8)	1.369 (11)	C(10)—C(11)	1.341 (14)
C(7)—C(12)	1.390 (6)	C(10)—C(9)	1.380 (9)
C(6)—C(13)	1.473 (6)	C(25)—C(24)	1.356 (7)
C(2)—C(21)	1.486 (6)	C(11)—C(12)	1.389 (11)
O(2)—C(20)	1.220 (7)	C(24)—C(23)	1.374 (8)
C(26)—C(21)	1.376 (7)	C(16)—C(15)	1.362 (7)
C(26)—C(25)	1.384 (7)		
C(6)—O(3)—C(2)	118.6 (3)	C(21)—C(22)—C(23)	120.2 (5)
C(4)—C(5)—C(6)	122.4 (4)	C(2)—C(21)—C(26)	121.0 (4)
C(4)—C(5)—C(20)	115.9 (4)	C(2)—C(21)—C(22)	120.6 (4)
C(6)—C(5)—C(20)	121.5 (4)	C(26)—C(21)—C(22)	118.4 (4)
C(4)—C(3)—C(2)	120.9 (5)	C(13)—C(14)—C(15)	120.6 (4)
C(4)—C(3)—C(19)	117.2 (4)	C(13)—C(18)—C(17)	119.8 (5)
C(2)—C(3)—C(19)	121.7 (4)	C(6)—C(13)—C(14)	122.6 (4)
C(4)—C(7)—C(8)	121.9 (4)	C(6)—C(13)—C(18)	118.7 (4)
C(4)—C(7)—C(12)	119.8 (6)	C(14)—C(13)—C(18)	118.7 (4)
C(8)—C(7)—C(12)	118.2 (6)	C(18)—C(17)—C(16)	120.2 (5)
C(5)—C(4)—C(3)	108.5 (3)	C(7)—C(8)—C(9)	120.8 (5)
C(5)—C(4)—C(7)	111.6 (5)	C(11)—C(10)—C(9)	118.1 (7)
C(3)—C(4)—C(7)	112.0 (4)	C(26)—C(25)—C(24)	120.0 (5)
O(3)—C(6)—C(5)	120.9 (4)	C(10)—C(11)—C(12)	122.2 (6)
O(3)—C(6)—C(13)	110.1 (3)	C(25)—C(24)—C(23)	120.1 (5)
C(5)—C(6)—C(13)	128.9 (4)	C(22)—C(23)—C(24)	120.2 (4)
O(3)—C(2)—C(3)	122.3 (4)	C(17)—C(16)—C(15)	120.7 (5)
O(3)—C(2)—C(21)	110.1 (4)	C(3)—C(19)—O(1)	124.7 (5)
C(3)—C(2)—C(21)	127.6 (5)	C(7)—C(12)—C(11)	119.6 (7)
C(5)—C(20)—O(2)	122.9 (5)	C(14)—C(15)—C(16)	119.9 (5)
C(21)—C(26)—C(25)	121.1 (4)	C(8)—C(9)—C(10)	121.1 (7)

Data were collected with a variable scan rate and a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *XP* (Siemens, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bellanato, J., Florencio, F., García-Blanco, S., Martin, N. & Seoane, C. (1987). *J. Mol. Struct.* **162**, 19–30.

Bellanato, J., Florencio, F., Martin, N. & Seoane, C. (1988). *J. Mol. Struct.* **172**, 63–72.

Florencio, F. & García-Blanco, S. (1987). *Acta Cryst.* C**43**, 1430–1432.

Lokaj, L., Kettmann, V., Pavelčík, F., Ilavský, D. & Marchalín, Š. (1990). *Acta Cryst.* C**46**, 788–791.

Murugesan, R., Selladurai, S., Subramanian, K., Velmurugan, D., Hamilton, J. R., Chen, Y.-S., Schapiro, P. J. & Narasinga Rao, S. (1996). *Acta Cryst.* C**52**, 2318–2320.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 2601-2607

Four Diterpene Isonitriles from the Sponge *Cymbastela hooperi*

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Abstract

The low-temperature X-ray structures of four isomeric diterpene isonitriles, $C_{21}H_{31}N$, obtained from the sponge *Cymbastela hooperi*, are reported. These are the tetracyclic compounds, (1*S**,3*S**,4*R**,7*S**,8*S**,12*S**,13*S**)-7-isocyanocycloamphilect-11(20)-ene (alternative name: 1,4,7,7-tetramethyl-1,2,3,3a,4,5,5a,6,7,9,10,10a,10b,10c-tetradecahydropyrenyl 1-isocyanide) and (1*S**,3*S**,-4*R**,7*S**,8*S**,11*R**,12*R**,13*S**,20*S**)-7-isocyanoisocycloamphilect-14-ene (alternative name: 1,4,7,8-tetramethyl-1,2,3,3a,4,5,5a,8,8a,9,10,10a,10b,10c-tetradecahydropyrenyl 1-isocyanide), and the tricyclic compounds, (1*S**,3*S**,4*R**,7*S**,8*S**,12*S**,13*S**)-7-isocyanoamphilecta-11(20),15-diene [alternative name: 1,4-dimethyl-7-methylene-6-(2-methyl-2-propenyl)perhydro-1*H*-phenalenyl 1-isocyanide] and (1*R**,3*S**,4*R**,7*S**,8*S**,-13*R**)-7-isocyanoamphilecta-11,14-diene [alternative name: 1,4,7-trimethyl-6-(2-methyl-1-propenyl)-2,3,3a,-4,5,6,8,9,9a,9b-decahydro-1*H*-phenalenyl 1-isocyanide]. All of the structures exhibit *trans*-fused ring systems.

Comment

Naturally occurring isonitriles are relatively rare, although diterpene isonitriles are often found in sponges (Baker, Wells, Oberhänsli & Hawes, 1976; Wratten, Faulkner, Hirotsu & Clardy, 1978; Kazlauskas, Murphy,

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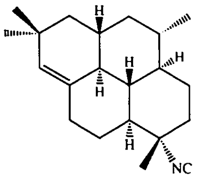
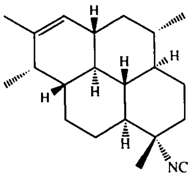
Wells & Blount, 1980; Chang, Patra, Baker & Scheuer, 1987; Molinski, Faulkner, Van Duyne & Clardy, 1987; Omar, Albert, Fanni & Crews, 1988; Sharma *et al.*, 1992). The X-ray crystal structures of nine diterpene isonitriles have been reported (Baker *et al.*, 1976; Wratten *et al.*, 1978; Kazlauskas *et al.*, 1980; Molinski *et al.*, 1987; Sharma *et al.*, 1992), as well as the absolute configuration determination of a derivative of one of them (Fookes, Garson, MacLeod, Skelton & White, 1988). A series of novel marine diterpene metabolites, 12 in all, has been isolated from the tropical marine sponge *Cymbastela hooperi* van Soest, Desqueyroux–Faundez, Wright and König (Axinellidae, Halichondrida) and characterized by König, Wright & Angerhofer (1996), who also found that all of these compounds exhibit varying degrees of *in vitro* antimalarial activity. Since several of these were crystalline and their relative configurations had not been established unambiguously, we have undertaken the X-ray crystallographic analyses and determined the structures of four compounds to be (1S*,3S*,4R*,7S*,8S*,12S*,13S*)-7-isocyanocycloamphilect-11(20)-ene, (I), (1S*,3S*,4R*,7S*,8S*,11R*,12R*,13S*,20S*)-7-isocyanoisocycloamphilect-14-ene, (II), (1S*,3S*,4R*,7S*,8S*,12S*,13S*)-7-isocyanoamphilecta-11(20),15-diene, (III), and (1R*,3S*,4R*,7S*,8S*,13R*)-7-isocyanoamphilecta-11,14-diene, (IV). Semisystematic compound names have been used in order to maintain consistency and facilitate comparisons both with previous work and between the compounds reported here.


(I)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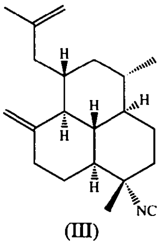
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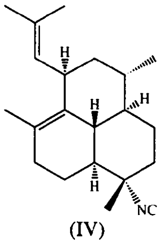
(IV)

Views of compounds (I)–(III) and molecule *A* of (IV), showing the displacement ellipsoids and the atomic numbering schemes, are shown in Fig. 1. Most of the bond lengths and angles within each structure correspond to the expected values, and the ring distortions introduced by the cyclohexene double bonds in (I), (II) and (IV) do not lead to any exceptional geometries. In each structure, the C(7)—C(8) bond adjacent to the nitrile group is elongated, reaching a maximum of 1.552 (4) Å in compound (II). The bonds about C(13), particularly for compound (III), are also consistently longer than the other C—C bonds. Compound (IV) has three independent molecules in the asymmetric unit. *MISSYM* (Le Page, 1988) did not reveal any overlooked symmetry, although molecules *A* and *C* are closely related by a pseudo-twofold screw axis parallel to the *a* axis at $y = 0.63$, $z = 0.75$. The independent molecules of (IV) are all of the same enantiomorph and the only significant differences between their geometries are twists of up to 20° about the C(1)—C(14) bond which links the isobutenyl substituent to the ring system, as well as small distortions of up to 6° in the torsion angles involving the cyclohexane ring to which the isobutenyl substituent is bonded. The nitrile C atom is involved in the shortest intermolecular contacts in each structure. This is probably caused by the charge distribution within the nitrile group shrinking the electron cloud about the C atom and reducing its effective radius. The shortest C(21)···H contacts in compounds (I)–(IV) are 0.33 (2), 0.08, 0.08 (2) and 0.02 Å, respectively, shorter than the sum of the van der Waals radii.

The absolute configuration of each structure has not been determined, however, the configuration has been chosen in each case so that the stereochemistries at C(3) and C(7) correspond with those at the same chiral centres in a derivative of the related compound diisocyanoadociane, for which the absolute configuration has been determined (Fookes *et al.*, 1988). Such an assumption, while reasonable, should not be taken as a definitive assignment of the absolute configuration of these compounds.

The four structures are isomeric and intimately related to each other and to the structures of a number of other diterpene isonitriles. Compounds (I) and (II) are tetracyclic compounds, while (III) and (IV) are tricyclic compounds in which the fourth ring has not been closed, giving rise, in (III), to an isobutenyl substituent at C(1) and an *exo*-methylene group at C(11). In compound (IV), there is an isobutenyl group at C(1) and the *exo* double bond of compound (III) has migrated to C(11)=C(12).

The structure of compound (II) can be derived from that of 7,15-diisocyanoadociane (Kazlauskas *et al.*, 1980) if the 15-isocyano substituent in the latter is removed with the subsequent formation of a cyclohexene double bond at the same site. Compound (III) might actually be the compound reported as 7-isocyanoepiamphilecta-11(20),15-diene by Kazlauskas *et al.* (1980). For the latter compound, the inverse stereochemistry was indicated at C(1) but the stereochemistry had only been mooted, the proposed structure being based only on spectroscopic data and the relative configuration obtained from their X-ray structure determination of the isomer, 7-isocyanoepiamphilecta-11(20),14-diene. That a variation in the relative stereochemistry at C(1) is possible for these

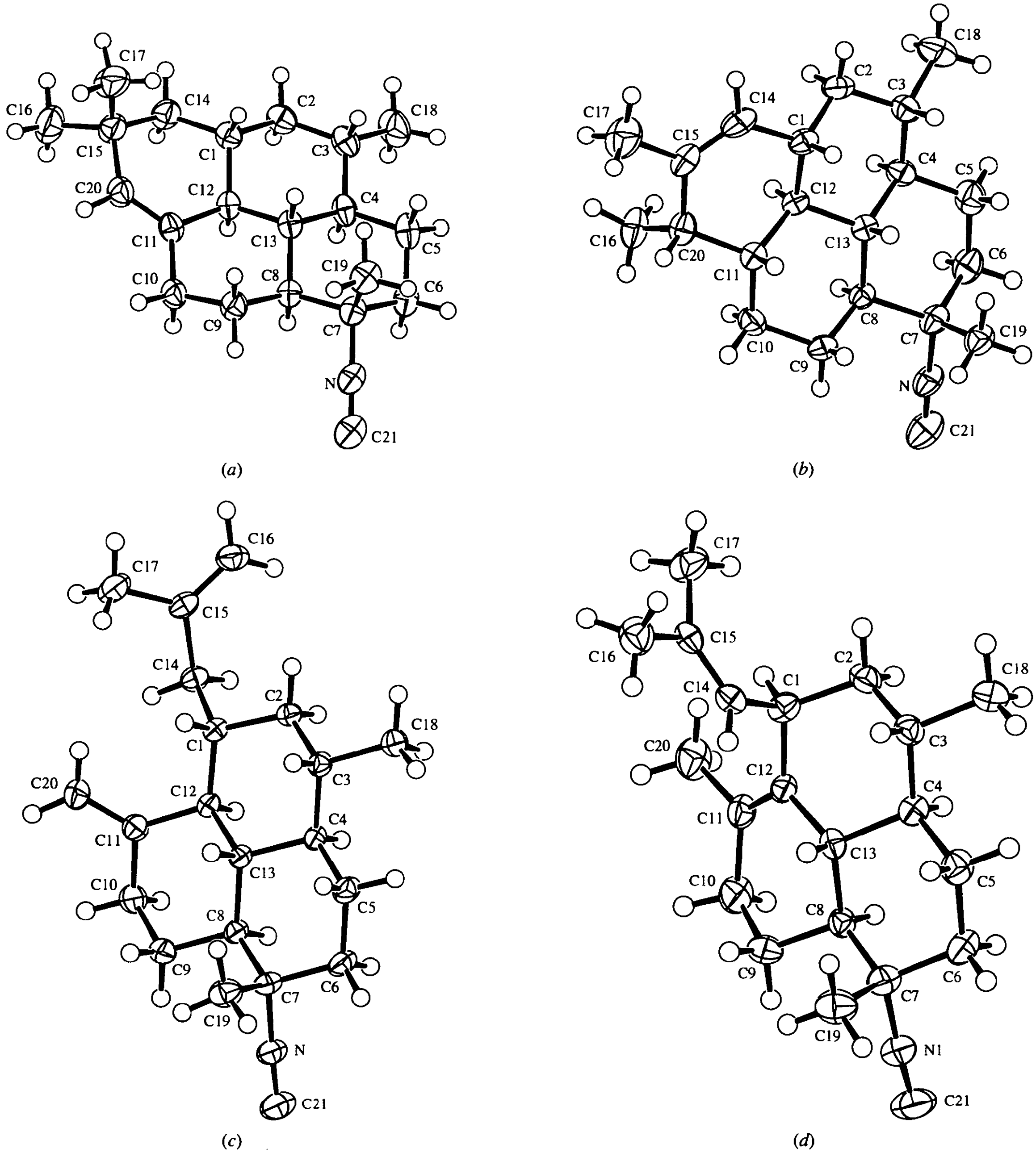

Fig. 1. Views (*a*)–(*d*) of the molecules of compounds (I)–(III) and molecule *A* of compound (IV), respectively, showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary size.

compounds is shown by the structure of (IV), which has the inverse configuration at C(1) relative to that in (III). Compound (IV), therefore, has the same overall structure and relative configuration as 7-isocyano-epiamphilecta-11(20),14-diene, with the exception that the *exo*-methylene bond in the latter has migrated to become the *endo*-methylene bond at C(11)=C(12) in (IV).

The puckering parameters, θ and φ_2 (Cremer & Pople, 1975) (Table 9), show that the cyclohexane rings in each structure adopt chair conformations, while the cyclohexene rings have half-chair conformations (Boeyens, 1978). Those cyclohexane rings which are fused to a cyclohexene ring are slightly distorted from the ideal chair conformation (θ = 0°) whereas in compound (III), which does not possess a cyclohexene ring, the θ parameters are much closer to the ideal value. All rings are *trans* fused, which results in relatively flat molecules. The same arrangement was observed for diisocyanoadociane (Baker *et al.*, 1976;

Fookes *et al.*, 1988), 8,15-diisocyanoamphilect-11(20)-ene (Wratten *et al.*, 1978), 7-isocyanoepiamphilecta-11(20),14-diene, 8-isocyanocycloamphilect-10-ene and 7,15-diisocyanoadociane (Kazlauskas *et al.*, 1980). In contrast, 7-isocyanocycloamphilect-1-ene, 7-isocyanoamphilect-11-ene (Molinski *et al.*, 1987) and 7-isocyanoneoamphilecta-11,15-diene (Sharma *et al.*, 1992) have *cis*-fused ring junctions.

Experimental

Compounds (I)–(IV) were isolated from the tropical marine sponge *Cymbastela hooperi* (König, Wright & Angerhofer, 1996). Suitable crystals were obtained in each case by recrystallization from hexane.

Compound (I)

Crystal data

$C_{21}H_{31}N$
$M_r = 297.48$
Orthorhombic
$P2_12_12_1$
$a = 12.960 (2)$ Å
$b = 17.444 (3)$ Å
$c = 8.068 (2)$ Å
$V = 1824.0 (6)$ Å^3
$Z = 4$
$D_x = 1.083$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 18.0$–$19.5°$
$\mu = 0.0615$ mm^{-1}
$T = 173 (1)$ K
Prism
0.47 × 0.35 × 0.27 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7208 measured reflections
5318 independent reflections
3970 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 18$
$k = -1 \rightarrow 24$
$l = -1 \rightarrow 11$
3 standard reflections monitored every 150 reflections intensity decay: not significant

Refinement

Refinement on F
$R = 0.0466$
$wR = 0.0410$
$S = 1.706$
3970 reflections
324 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{\rm max} = 0.0003$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $g = 2 (1) \times 10^{-7}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N	0.6220 (1)	0.07116 (8)	1.1792 (2)	0.0395 (5)
C(1)	0.3524 (1)	0.08045 (9)	0.5354 (2)	0.0361 (5)
C(2)	0.3668 (2)	−0.00379 (9)	0.4894 (3)	0.0412 (6)
C(3)	0.4689 (1)	−0.0381 (1)	0.5504 (3)	0.0410 (6)
C(4)	0.4886 (1)	−0.02102 (9)	0.7344 (2)	0.0351 (5)
C(5)	0.5959 (1)	−0.0480 (1)	0.7899 (3)	0.0451 (6)
C(6)	0.6185 (1)	−0.0279 (1)	0.9703 (3)	0.0424 (6)
C(7)	0.6082 (1)	0.05852 (9)	1.0009 (2)	0.0353 (5)
C(8)	0.4978 (1)	0.08467 (9)	0.9552 (2)	0.0309 (4)
C(9)	0.4768 (1)	0.16925 (9)	0.9897 (3)	0.0378 (5)
C(10)	0.3627 (1)	0.1871 (1)	0.9578 (2)	0.0394 (5)
C(11)	0.3319 (1)	0.16809 (9)	0.7828 (2)	0.0340 (5)
C(12)	0.3638 (1)	0.08926 (8)	0.7233 (2)	0.0308 (4)
C(13)	0.4739 (1)	0.06512 (8)	0.7732 (2)	0.0300 (4)
C(14)	0.2493 (1)	0.1130 (1)	0.4784 (3)	0.0424 (6)
C(15)	0.2358 (1)	0.1987 (1)	0.5177 (2)	0.0447 (6)
C(16)	0.1208 (2)	0.2194 (2)	0.5080 (4)	0.0655 (9)
C(17)	0.2962 (2)	0.2485 (1)	0.3942 (3)	0.0614 (9)
C(18)	0.4706 (2)	−0.1244 (1)	0.5122 (4)	0.0602 (8)
C(19)	0.6936 (1)	0.1043 (1)	0.9145 (3)	0.0449 (6)
C(20)	0.2755 (1)	0.2151 (1)	0.6903 (2)	0.0406 (5)
C(21)	0.6348 (1)	0.0827 (1)	1.3186 (3)	0.0485 (6)

Table 2. *Selected geometric parameters (Å, °) for (I)*

N—C(7)	1.466 (2)	C(10)—C(11)	1.504 (2)
N—C(21)	1.154 (2)	C(11)—C(12)	1.514 (2)
C(4)—C(13)	1.546 (2)	C(11)—C(20)	1.328 (2)
C(7)—C(8)	1.546 (2)	C(12)—C(13)	1.542 (2)
C(8)—C(13)	1.539 (2)	C(15)—C(20)	1.512 (2)
C(7)—N—C(21)	178.1 (2)	C(12)—C(11)—C(20)	122.2 (2)
C(10)—C(11)—C(12)	115.2 (1)	C(11)—C(20)—C(15)	126.0 (2)
C(10)—C(11)—C(20)	122.5 (2)		

Compound (II)

Crystal data

$C_{21}H_{31}N$
$M_r = 297.48$
Orthorhombic
$P2_12_12_1$
$a = 14.319 (2)$ Å
$b = 17.591 (4)$ Å
$c = 7.145 (2)$ Å
$V = 1799.8 (6)$ Å^3
$Z = 4$
$D_x = 1.098$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 17.5$–$20.0°$
$\mu = 0.0623$ mm^{-1}
$T = 173 (1)$ K
Prism
0.40 × 0.40 × 0.33 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3607 measured reflections
3468 independent reflections
2219 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 20$
$k = -1 \rightarrow 24$
$l = -1 \rightarrow 10$
3 standard reflections monitored every 150 reflections intensity decay: not significant

Refinement

Refinement on F
$R = 0.0564$
$wR = 0.0431$
$S = 2.091$
2219 reflections
230 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{\rm max} = 0.0002$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

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

	x	y	z	U_{eq}
N	0.6518 (2)	0.1726 (2)	1.1542 (4)	0.037 (1)
C(1)	0.9375 (2)	0.1292 (2)	0.4982 (5)	0.032 (1)
C(2)	0.9401 (2)	0.2121 (2)	0.4373 (5)	0.038 (1)
C(3)	0.8479 (2)	0.2532 (2)	0.4756 (5)	0.038 (1)
C(4)	0.8158 (2)	0.2434 (2)	0.6801 (5)	0.033 (1)
C(5)	0.7202 (2)	0.2798 (2)	0.7166 (6)	0.043 (1)
C(6)	0.6832 (2)	0.2648 (2)	0.9130 (5)	0.042 (1)
C(7)	0.6791 (2)	0.1799 (2)	0.9577 (5)	0.033 (1)
C(8)	0.7784 (2)	0.1456 (2)	0.9358 (5)	0.027 (1)
C(9)	0.7847 (2)	0.0623 (2)	0.9911 (5)	0.036 (1)
C(10)	0.8855 (2)	0.0337 (2)	0.9751 (5)	0.037 (1)
C(11)	0.9216 (2)	0.0420 (2)	0.7756 (5)	0.0287 (9)
C(12)	0.9127 (2)	0.1236 (2)	0.7069 (4)	0.0264 (9)
C(13)	0.8152 (2)	0.1584 (2)	0.7359 (5)	0.0263 (9)
C(14)	1.0239 (2)	0.0842 (2)	0.4531 (5)	0.045 (1)
C(15)	1.0608 (2)	0.0309 (2)	0.5603 (5)	0.035 (1)
C(16)	1.0899 (2)	0.0396 (2)	0.9037 (6)	0.048 (1)
C(17)	1.1441 (3)	−0.0140 (3)	0.4957 (7)	0.064 (2)
C(18)	0.8559 (3)	0.3373 (2)	0.4190 (7)	0.065 (2)
C(19)	0.6028 (2)	0.1396 (2)	0.8447 (5)	0.038 (1)
C(20)	1.0224 (2)	0.0125 (2)	0.7501 (6)	0.035 (1)
C(21)	0.6277 (3)	0.1656 (2)	1.3069 (6)	0.052 (1)

Table 4. *Selected geometric parameters (Å, °) for (II)*

N—C(7)	1.464 (4)	C(8)—C(13)	1.539 (4)
N—C(21)	1.151 (4)	C(12)—C(13)	1.539 (4)
C(1)—C(14)	1.503 (4)	C(14)—C(15)	1.321 (5)
C(4)—C(13)	1.547 (4)	C(15)—C(17)	1.502 (4)
C(7)—C(8)	1.552 (4)	C(15)—C(20)	1.499 (5)
C(7)—N—C(21)	177.7 (4)	C(14)—C(15)—C(20)	122.0 (3)
C(1)—C(14)—C(15)	125.3 (3)	C(17)—C(15)—C(20)	117.1 (3)
C(14)—C(15)—C(17)	120.8 (4)		

Compound (III)

Crystal data

$C_{21}H_{31}N$
$M_r = 297.48$
Monoclinic
$P2_1$
$a = 9.502$ (1) Å
$b = 9.942$ (1) Å
$c = 9.841$ (2) Å
$\beta = 106.60$ (1)°
$V = 890.9$ (2) Å^3
$Z = 2$
$D_x = 1.109$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 18.5$–20.0°
$\mu = 0.0629$ mm^{-1}
$T = 173$ (1) K
Prism
0.50 × 0.45 × 0.40 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2878 measured reflections
2730 independent reflections
2379 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.013$

$\theta_{max} = 30$°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 150 reflections
intensity decay: not significant

Refinement

Refinement on F
$R = 0.0393$
$wR = 0.0374$
$S = 2.008$
2379 reflections
323 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{max} = 0.0002$

$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $g = 5$ (3) × 10^{-7}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

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

	x	y	z	U_{eq}
N	0.2062 (2)	0.80487	0.5404 (2)	0.0321 (5)
C(1)	0.2923 (2)	0.3407 (2)	0.1301 (2)	0.0231 (5)
C(2)	0.2616 (2)	0.4384 (3)	0.0041 (2)	0.0248 (6)
C(3)	0.1477 (2)	0.5470 (3)	0.0035 (2)	0.0249 (6)
C(4)	0.1925 (2)	0.6249 (3)	0.1439 (2)	0.0228 (5)
C(5)	0.0832 (2)	0.7364 (3)	0.1480 (2)	0.0305 (6)
C(6)	0.1285 (2)	0.8145 (3)	0.2869 (2)	0.0312 (6)
C(7)	0.1457 (2)	0.7215 (3)	0.4148 (2)	0.0277 (6)
C(8)	0.2583 (2)	0.6091 (3)	0.4132 (2)	0.0237 (5)
C(9)	0.2866 (2)	0.5167 (3)	0.5430 (2)	0.0317 (6)
C(10)	0.3998 (2)	0.4078 (3)	0.5390 (2)	0.0337 (7)
C(11)	0.3450 (2)	0.3296 (3)	0.4022 (2)	0.0281 (6)
C(12)	0.3288 (2)	0.4173 (3)	0.2719 (2)	0.0222 (5)
C(13)	0.2137 (2)	0.5293 (3)	0.2719 (2)	0.0215 (5)
C(14)	0.4191 (2)	0.2458 (3)	0.1223 (2)	0.0271 (6)
C(15)	0.3757 (2)	0.1457 (3)	0.0023 (2)	0.0286 (6)
C(16)	0.4003 (3)	0.1662 (3)	−0.1217 (2)	0.0373 (7)
C(17)	0.3004 (3)	0.0207 (3)	0.0310 (3)	0.0426 (8)
C(18)	0.1306 (3)	0.6382 (3)	−0.1260 (2)	0.0349 (7)
C(19)	−0.0031 (2)	0.6697 (3)	0.4239 (2)	0.0362 (7)
C(20)	0.3037 (3)	0.2025 (3)	0.4021 (3)	0.0355 (7)
C(21)	0.2495 (3)	0.8760 (3)	0.6354 (2)	0.0443 (8)

Table 6. *Selected geometric parameters (Å, °) for (III)*

N—C(7)	1.463 (2)	C(11)—C(12)	1.521 (2)
N—C(21)	1.151 (3)	C(11)—C(20)	1.323 (3)
C(4)—C(13)	1.544 (2)	C(12)—C(13)	1.561 (2)
C(7)—C(8)	1.550 (2)	C(14)—C(15)	1.508 (3)
C(8)—C(13)	1.551 (2)	C(15)—C(16)	1.322 (3)
C(10)—C(11)	1.512 (3)	C(15)—C(17)	1.501 (3)
C(7)—N—C(21)	176.4 (2)	C(1)—C(14)—C(15)	113.4 (1)
C(10)—C(11)—C(12)	112.5 (2)	C(14)—C(15)—C(16)	122.7 (2)
C(10)—C(11)—C(20)	121.2 (2)	C(14)—C(15)—C(17)	115.9 (2)
C(12)—C(11)—C(20)	126.0 (2)	C(16)—C(15)—C(17)	121.4 (2)

Compound (IV)

Crystal data

$C_{21}H_{31}N$
$M_r = 297.48$
Orthorhombic
$P2_12_12$
$a = 20.380$ (6) Å
$b = 32.683$ (9) Å
$c = 8.370$ (7) Å
$V = 5575$ (5) Å^3
$Z = 12$
$D_x = 1.063$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.0$–17.5°
$\mu = 0.0603$ mm^{-1}
$T = 173$ (1) K
Prism
0.37 × 0.35 × 0.25 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: none
8289 measured reflections
8100 independent reflections
4453 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.028$

$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 26$
$k = -1 \rightarrow 42$
$l = -1 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity decay: not significant

Refinement

Refinement on *F*
$R = 0.0573$
$wR = 0.0459$
$S = 1.711$
4453 reflections
595 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$

$(\Delta/\sigma)_{\rm max} = 0.0003$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (IV)*

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

	x	*y*	*z*	$U_{\rm eq}$
N(1)	0.7181 (2)	0.7975 (1)	1.1098 (6)	0.039 (2)
C(1)	0.4993 (2)	0.7226 (1)	0.6683 (6)	0.030 (2)
C(2)	0.5512 (2)	0.7015 (1)	0.5635 (6)	0.032 (2)
C(3)	0.6114 (2)	0.7288 (1)	0.5328 (6)	0.029 (2)
C(4)	0.6418 (2)	0.7398 (1)	0.6935 (6)	0.027 (2)
C(5)	0.7030 (2)	0.7669 (2)	0.6762 (6)	0.036 (2)
C(6)	0.7342 (2)	0.7773 (2)	0.8362 (7)	0.037 (2)
C(7)	0.6857 (2)	0.7963 (2)	0.9535 (7)	0.036 (2)
C(8)	0.6249 (2)	0.7684 (1)	0.9700 (6)	0.026 (2)
C(9)	0.5740 (2)	0.7829 (2)	1.0902 (6)	0.038 (2)
C(10)	0.5227 (2)	0.7497 (2)	1.1171 (6)	0.043 (2)
C(11)	0.4973 (2)	0.7317 (2)	0.9640 (6)	0.032 (2)
C(12)	0.5274 (2)	0.7373 (1)	0.8237 (6)	0.027 (2)
C(13)	0.5922 (2)	0.7607 (1)	0.8081 (6)	0.026 (2)
C(14)	0.4654 (2)	0.7579 (1)	0.5806 (6)	0.028 (2)
C(15)	0.4124 (2)	0.7545 (1)	0.4901 (6)	0.029 (2)
C(16)	0.3817 (2)	0.7912 (2)	0.4125 (7)	0.042 (2)
C(17)	0.3780 (2)	0.7150 (2)	0.4580 (7)	0.044 (2)
C(18)	0.6601 (2)	0.7065 (2)	0.4225 (7)	0.041 (2)
C(19)	0.6694 (3)	0.8411 (2)	0.9106 (7)	0.044 (2)
C(20)	0.4343 (3)	0.7079 (2)	0.9850 (7)	0.045 (2)
C(21)	0.7452 (3)	0.7972 (2)	1.2302 (7)	0.053 (2)
N(2)	0.7831 (2)	0.6504 (1)	0.9135 (6)	0.038 (2)
C(31)	0.9973 (2)	0.5663 (1)	1.3461 (6)	0.033 (2)
C(32)	0.9445 (2)	0.5467 (1)	1.4510 (6)	0.037 (2)
C(33)	0.8853 (2)	0.5741 (1)	1.4819 (6)	0.036 (2)
C(34)	0.8559 (2)	0.5880 (1)	1.3227 (6)	0.030 (2)
C(35)	0.7984 (2)	0.6175 (2)	1.3450 (7)	0.038 (2)
C(36)	0.7670 (2)	0.6296 (2)	1.1858 (7)	0.037 (2)
C(37)	0.8165 (2)	0.6477 (1)	1.0679 (6)	0.032 (2)
C(38)	0.8744 (2)	0.6176 (1)	1.0478 (6)	0.030 (2)
C(39)	0.9262 (2)	0.6311 (2)	0.9281 (7)	0.046 (2)
C(40)	0.9736 (2)	0.5959 (2)	0.8977 (7)	0.054 (2)
C(41)	0.9976 (3)	0.5761 (2)	1.0492 (6)	0.041 (2)
C(42)	0.9692 (2)	0.5821 (1)	1.1901 (6)	0.030 (2)
C(43)	0.9062 (2)	0.6079 (1)	1.2109 (6)	0.027 (2)
C(44)	1.0323 (2)	0.6003 (1)	1.4325 (6)	0.034 (2)
C(45)	1.0932 (3)	0.6007 (2)	1.4894 (7)	0.042 (2)
C(46)	1.1206 (3)	0.6366 (2)	1.5800 (7)	0.054 (2)
C(47)	1.1403 (3)	0.5660 (2)	1.474 (1)	0.110 (4)
C(48)	0.8355 (2)	0.5522 (2)	1.5893 (7)	0.052 (2)
C(49)	0.8369 (2)	0.6914 (1)	1.1153 (7)	0.042 (2)
C(50)	1.0579 (3)	0.5499 (2)	1.0229 (7)	0.060 (2)
C(51)	0.7569 (3)	0.6506 (2)	0.7923 (7)	0.045 (2)
N(3)	0.6481 (2)	0.3949 (1)	0.3957 (6)	0.040 (2)
C(61)	0.6476 (2)	0.5508 (1)	0.8370 (6)	0.035 (2)
C(62)	0.7012 (2)	0.5325 (2)	0.9435 (7)	0.040 (2)
C(63)	0.6954 (2)	0.4865 (1)	0.9708 (6)	0.033 (2)
C(64)	0.6945 (2)	0.4646 (1)	0.8098 (6)	0.032 (2)
C(65)	0.6871 (2)	0.4184 (2)	0.8281 (7)	0.040 (2)
C(66)	0.6864 (2)	0.3963 (1)	0.6665 (7)	0.038 (2)
C(67)	0.6350 (2)	0.4126 (1)	0.5534 (7)	0.033 (2)
C(68)	0.6429 (2)	0.4596 (1)	0.5363 (6)	0.030 (2)
C(69)	0.5946 (2)	0.4791 (2)	0.4196 (7)	0.039 (2)
C(70)	0.6142 (3)	0.5237 (2)	0.3909 (7)	0.041 (2)
C(71)	0.6285 (2)	0.5465 (1)	0.5414 (7)	0.033 (2)
C(72)	0.6398 (2)	0.5272 (1)	0.6799 (6)	0.028 (2)
C(73)	0.6397 (2)	0.4808 (1)	0.7000 (6)	0.028 (2)
C(74)	0.5823 (2)	0.5537 (2)	0.9248 (6)	0.037 (2)
C(75)	0.5563 (2)	0.5861 (2)	0.9931 (6)	0.035 (2)
C(76)	0.4913 (3)	0.5837 (2)	1.0771 (6)	0.049 (2)
C(77)	0.5864 (3)	0.6279 (2)	0.9953 (7)	0.053 (2)
C(78)	0.7505 (3)	0.4722 (2)	1.0825 (7)	0.055 (2)
C(79)	0.5641 (2)	0.3995 (1)	0.6019 (7)	0.045 (2)
C(80)	0.6261 (2)	0.5924 (2)	0.5223 (7)	0.047 (2)
C(81)	0.6608 (3)	0.3805 (2)	0.2745 (8)	0.054 (2)

Table 8. *Selected geometric parameters (Å, °) for (IV)*

	Molecule *A*	Molecule *B*	Molecule *C*
N(1)—C(7)	1.466 (7)	1.464 (7)	1.466 (7)
N(1)—C(21)	1.150 (6)	1.146 (6)	1.148 (7)
C(1)—C(12)	1.499 (6)	1.515 (7)	1.532 (7)
C(1)—C(14)	1.530 (6)	1.507 (6)	1.524 (6)
C(4)—C(13)	1.552 (6)	1.534 (6)	1.541 (6)
C(7)—C(8)	1.544 (6)	1.546 (6)	1.550 (6)
C(8)—C(13)	1.531 (6)	1.544 (6)	1.538 (6)
C(10)—C(11)	1.502 (7)	1.506 (7)	1.492 (7)
C(11)—C(12)	1.337 (6)	1.329 (7)	1.340 (7)
C(11)—C(20)	1.511 (6)	1.516 (7)	1.509 (6)
C(12)—C(13)	1.532 (6)	1.547 (6)	1.526 (6)
C(14)—C(15)	1.324 (6)	1.329 (6)	1.316 (6)
C(15)—C(16)	1.501 (6)	1.505 (7)	1.501 (6)
C(15)—C(17)	1.496 (6)	1.492 (7)	1.496 (6)
C(7)—N(1)—C(21)	177.1 (6)	176.9 (6)	177.2 (6)
C(10)—C(11)—C(12)	122.5 (4)	122.9 (5)	122.0 (4)
C(10)—C(11)—C(20)	113.2 (4)	112.7 (5)	113.6 (5)
C(12)—C(11)—C(20)	124.2 (5)	124.4 (5)	124.4 (5)
C(1)—C(12)—C(11)	122.9 (4)	123.4 (4)	121.6 (4)
C(1)—C(12)—C(13)	114.5 (4)	113.7 (4)	113.9 (4)
C(11)—C(12)—C(13)	122.6 (5)	122.8 (5)	124.2 (5)
C(1)—C(14)—C(15)	125.6 (4)	128.4 (5)	127.7 (4)
C(14)—C(15)—C(16)	121.5 (4)	122.2 (5)	121.1 (5)
C(14)—C(15)—C(17)	123.8 (4)	124.2 (5)	125.0 (5)
C(16)—C(15)—C(17)	114.7 (4)	113.6 (5)	113.9 (4)
C(1)—C(2)—C(3)—C(4)	59.1 (5)	55.7 (5)	56.1 (6)
C(1)—C(12)—C(13)—C(4)	−44.9 (5)	−47.0 (5)	−46.1 (6)
C(2)—C(1)—C(12)—C(11)	−135.0 (5)	−135.3 (5)	−140.9 (5)
C(2)—C(1)—C(12)—C(13)	47.1 (5)	48.0 (5)	44.4 (6)
C(2)—C(1)—C(14)—C(15)	88.4 (6)	108.1 (6)	99.8 (6)
C(2)—C(3)—C(4)—C(5)	179.7 (4)	−176.9 (4)	−178.6 (4)
C(2)—C(3)—C(4)—C(13)	−56.1 (5)	−53.5 (5)	−55.4 (5)
C(3)—C(2)—C(1)—C(12)	−55.1 (5)	−53.7 (6)	−50.7 (6)
C(3)—C(2)—C(1)—C(14)	69.6 (5)	70.0 (5)	74.1 (5)
C(4)—C(13)—C(12)—C(11)	137.2 (5)	136.3 (5)	139.4 (5)
C(11)—C(12)—C(1)—C(14)	99.4 (5)	100.2 (6)	93.9 (5)
C(12)—C(1)—C(14)—C(15)	−145.9 (5)	−127.2 (6)	−134.6 (5)
C(13)—C(12)—C(1)—C(14)	−78.5 (5)	−76.5 (5)	−80.8 (5)

Table 9. *Ring puckering parameters θ and φ_2 (°) for compounds (I)–(IV)*

	θ for rings containing atoms				φ_2 for the cyclohexene ring
	C(2)	C(5)	C(9)	C(14)	
(I)	10.6 (2)	4.4 (2)	14.0 (2)	49.5 (2)	334.2 (3)
(II)	7.7 (3)	6.3 (4)	7.6 (3)	46.7 (4)	91.9 (6)
(III)	4.2 (2)	0.0 (2)	4.7 (2)		

(IV*A*)	10.6 (5)	5.0 (5)	52.3 (6)		332.1 (7)
(IV*B*)	6.1 (5)	4.6 (5)	52.4 (6)		332.4 (8)
(IV*C*)	8.7 (6)	5.0 (5)	50.0 (6)		331.2 (8)

For compound (I), the data collection included the measurement of the Friedel mates of all reflections within the listed *hkl* range. For each compound, the H atoms were located in a difference electron-density map and for compounds (I) and (III), they were refined isotropically. For (II) and (IV), the positions were geometrically optimized and held fixed (C—H = 0.95 Å), while the isotropic displacement parameters of (II) were refined and those of (IV) were fixed at $1.2U_{\rm eq}$ of the parent C atom.

MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structures were solved using direct methods (*SHELXS*86; Sheldrick, 1990) and the molecular graphics were produced using *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and contact distances, together with 50% displacement ellipsoid plots of the *B* and *C* molecules of compound (IV) have been deposited with the IUCr (Reference: AB1372). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baker, J. T., Wells, R. J., Oberhänsli, W. E. & Hawes, G. B. (1976). *J. Am. Chem. Soc.* **98**, 4010–4012.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

Chang, C. W. J., Patra, A., Baker, J. A. & Scheuer, P. J. (1987). *J. Am. Chem. Soc.* **109**, 6119–6123.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Fookes, C. J. R., Garson, M. J., MacLeod, J. K., Skelton, B. W. & White, A. H. (1988). *J. Chem. Soc. Perkin Trans.* 1, pp. 1003–1011.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kazlauskas, R., Murphy, P. T., Wells, R. J. & Blount, J. F. (1980). *Tetrahedron Lett.* **21**, 315–318.

König, G. M., Wright, A. D. & Angerhofer, C. K. (1996). *J. Org. Chem.* **61**, 3259–3267.

Le Page, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molinski, T. F., Faulkner, D. J., Van Duyne, G. D. & Clardy, J. (1987). *J. Org. Chem.* **52**, 3334–3337.

Omar, S., Albert, C., Fanni, T. & Crews, P. (1988). *J. Org. Chem.* **53**, 5971–5972.

Sharma, H. A., Tanaka, J., Higa, T., Lithgow, A., Bernardinelli, G. & Jefford, C. W. (1992). *Tetrahedron Lett.* **33**, 1593–1596.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Wratten, S. J., Faulkner, D. J., Hirotsu, K. & Clardy, J. (1978). *Tetrahedron Lett.* **19**, 4345–4348.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1996). C**52**, 2607–2609

3-Hexanoyl-1-tosylindole. A Highly Stereospecific Preparation of 3-Alkyl-Substituted Indoles

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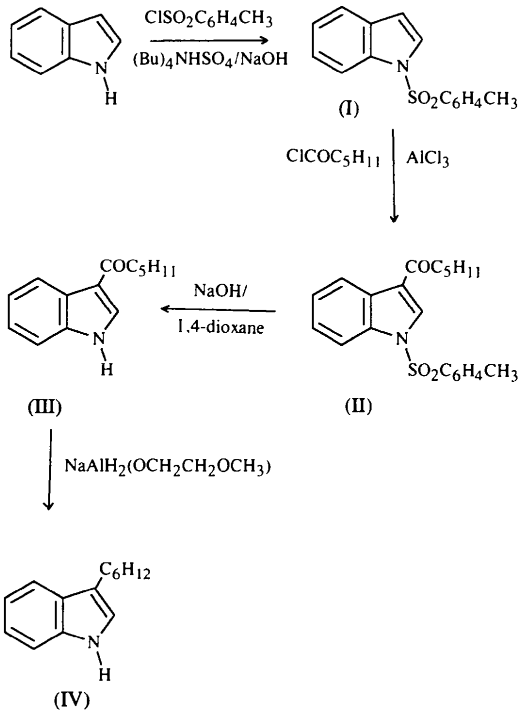
Abstract

The title molecule, 1-(1-tosyl-3-indolyl)-1-hexanone, $C_{21}H_{23}NO_3S$, is configured so that the indole moiety eclipses one sulfonyl O atom and the toluene ring the other. As expected, the hexanoyl O atom is almost coplanar with the delocalized indole system.

Comment

3-Alkylindoles carrying an alkyl substituent larger than ethyl were previously unknown. We therefore synthesized 3-hexylindole, (IV), *via* Friedel–Craft acylation of 1-tosylindole, (I), which gave 3-hexanoyl-1-tosylindole, (II), as an intermediate. This was followed by saponification of the tosyl group and reduction of the ketone. The high yield of 3-hexanoyl-1-tosylindole and



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