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3a,4,9,9a-Tetrahydro-2-methyl-4β-phenylbenz[*f*]isoindoline

By Peter Murray-Rust and Judith Murray-Rust

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

and David Middlemiss

Glaxo Group Research Ltd, Ware SG12 0DJ, Hertfordshire, England

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Abstract. $C_{19}H_{21}N$, $M_r = 263{\cdot}4$, monoclinic, $P2_1/c$, $a = 10{\cdot}72\,(3)$, $b = 16{\cdot}94\,(6)$, $c = 8{\cdot}65\,(3)$ Å, $\beta = 70{\cdot}00\,(3)^\circ$ from diffractometer measurements (Mo $K\bar{\alpha}$ radiation), $V = 1476{\cdot}1$ Å^3, $Z = 4$, $D_c = 1{\cdot}18$ Mg m^{-3}, $F(000) = 568$, $\mu = 0{\cdot}035$ mm^{-1}, approximate crystal dimensions $0{\cdot}25 \times 0{\cdot}45 \times 0{\cdot}50$ mm. The structure, which refined to $R = 0{\cdot}095$, consists of L-shaped molecules with the β configuration.

Introduction. Systematic absences (from precession photographs) $h0l$: l odd and $0k0$: k odd indicated space group $P2_1/c$. Data were collected for $h0$–$15l$ with $\theta_{\max} = 25^\circ$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\bar{\alpha}$ radiation). The crystal quality was poor, with a mosaic spread of $\sim 1{\cdot}5^\circ$. 2321 data were collected, of which 1350 unique reflexions with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections were applied and the data scaled by a Wilson plot; no corrections for extinction or absorption were made. The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976), which was used for all calculations. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Unweighted full-matrix least-squares refinement (including isotropic H atoms) converged at $R = 0{\cdot}095$ for 1350 observed reflexions ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). A difference map at this point revealed no significant features. In the final cycle all shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1, bond distances and angles in Table 2.*

Discussion. The title compound (II) was prepared by hydrogenolysis of the benzylic alcohol (I) and is one of a series of compounds showing analgesic activity (Middlemiss, 1975). The structure determination was undertaken to confirm that hydrogenolysis had occurred with inversion of configuration (Mitsui, Kudo & Kobayashi, 1969) and to determine the conformation

Table 1. *Fractional atomic coordinates* (×10^4, *for* H ×10^3) *with e.s.d.'s in parentheses*

	x	y	z
C(1)	6518 (6)	6345 (3)	−1424 (8)
C(2)	5895 (6)	6562 (3)	1701 (7)
C(3)	5715 (7)	5144 (4)	2784 (8)
C(4)	6345 (9)	4451 (5)	3087 (8)
C(5)	7640 (8)	4410 (5)	2722 (9)
C(6)	8415 (7)	5091 (5)	1980 (8)
C(7)	8591 (7)	6487 (4)	977 (9)
C(8)	8758 (7)	6409 (4)	−2034 (9)
C(9)	6664 (6)	6824 (4)	−27 (8)
C(10)	8219 (6)	6836 (4)	−393 (8)
C(11)	6425 (6)	5775 (4)	2095 (7)
C(12)	7852 (7)	5753 (4)	1674 (8)
C(13)	7960 (8)	5953 (4)	−4130 (8)
C(14)	4385 (5)	6589 (3)	2075 (7)
C(15)	3741 (6)	6096 (4)	1317 (8)
C(16)	2390 (7)	6153 (4)	1689 (9)
C(17)	1649 (6)	6692 (5)	2842 (10)
C(18)	2260 (7)	7165 (5)	3607 (9)
C(19)	3620 (7)	7116 (4)	3260 (9)
N(1)	7753 (6)	6479 (3)	−2792 (7)
H(1)	581 (5)	642 (3)	−186 (6)
H(2)	646 (5)	578 (3)	−113 (6)
H(3)	612 (5)	694 (3)	250 (6)
H(4)	468 (5)	513 (3)	318 (6)
H(5)	581 (5)	404 (3)	362 (6)
H(6)	811 (5)	399 (3)	291 (6)
H(7)	942 (5)	501 (3)	155 (6)
H(8)	848 (5)	688 (3)	182 (7)
H(9)	951 (5)	640 (3)	63 (6)
H(10)	896 (5)	590 (3)	−198 (6)
H(11)	961 (5)	664 (3)	−270 (6)
H(12)	634 (5)	737 (3)	−24 (6)
H(13)	857 (5)	739 (3)	−45 (6)
H(14)	703 (5)	605 (3)	−454 (6)
H(15)	789 (5)	542 (3)	−391 (6)
H(16)	893 (5)	603 (3)	−533 (6)
H(17)	430 (5)	571 (3)	63 (6)
H(18)	207 (5)	584 (3)	116 (6)
H(19)	77 (5)	668 (3)	307 (6)
H(20)	167 (5)	751 (3)	461 (6)
H(21)	407 (5)	747 (3)	385 (6)

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35156 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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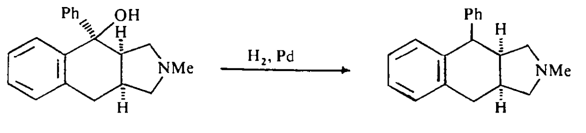
Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(9)	1·507 (10)	C(8)–C(10)	1·521 (10)
C(1)–N(1)	1·460 (7)	C(8)–N(1)	1·444 (11)
C(2)–C(9)	1·506 (8)	C(9)–C(10)	1·587 (9)
C(2)–C(11)	1·532 (9)	C(11)–C(12)	1·447 (9)
C(2)–C(14)	1·539 (8)	C(13)–N(1)	1·417 (9)
C(3)–C(4)	1·423 (11)	C(14)–C(15)	1·383 (10)
C(3)–C(11)	1·329 (9)	C(14)–C(19)	1·395 (8)
C(4)–C(5)	1·315 (13)	C(15)–C(16)	1·376 (9)
C(5)–C(6)	1·439 (11)	C(16)–C(17)	1·385 (10)
C(6)–C(12)	1·343 (11)	C(17)–C(18)	1·343 (12)
C(7)–C(10)	1·495 (11)	C(18)–C(19)	1·386 (10)
C(7)–C(12)	1·486 (10)		

N(1)–C(1)–C(9)	104·6 (5)	C(12)–C(11)–C(2)	114·0 (5)
C(11)–C(2)–C(9)	111·0 (4)	C(12)–C(11)–C(3)	119·1 (7)
C(14)–C(2)–C(9)	112·3 (6)	C(7)–C(12)–C(6)	124·4 (6)
C(14)–C(2)–C(11)	114·9 (5)	C(11)–C(12)–C(6)	118·7 (6)
C(11)–C(3)–C(4)	120·8 (7)	C(11)–C(12)–C(7)	116·8 (6)
C(5)–C(4)–C(3)	121·8 (7)	C(15)–C(14)–C(2)	122·8 (5)
C(6)–C(5)–C(4)	117·8 (8)	C(19)–C(14)–C(2)	119·0 (6)
C(12)–C(6)–C(5)	121·8 (7)	C(19)–C(14)–C(15)	118·1 (6)
C(12)–C(7)–C(10)	113·8 (7)	C(16)–C(15)–C(14)	120·2 (6)
N(1)–C(8)–C(10)	106·3 (5)	C(17)–C(16)–C(15)	120·9 (7)
C(2)–C(9)–C(1)	117·8 (5)	C(18)–C(17)–C(16)	119·5 (7)
C(10)–C(9)–C(1)	103·7 (5)	C(19)–C(18)–C(17)	120·8 (7)
C(10)–C(9)–C(2)	112·5 (6)	C(18)–C(19)–C(14)	120·5 (7)
C(8)–C(10)–C(7)	115·6 (6)	C(8)–N(1)–C(1)	103·3 (5)
C(9)–C(10)–C(7)	112·5 (5)	C(13)–N(1)–C(1)	114·2 (6)
C(9)–C(10)–C(8)	102·5 (6)	C(13)–N(1)–C(8)	112·7 (6)
C(3)–C(11)–C(2)	126·9 (6)		

of the molecule and the position of the N atom relative to the aromatic ring.



(I) (II)

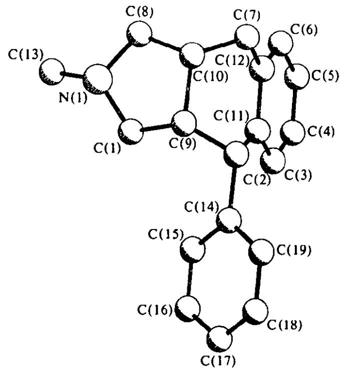


Fig. 1. A general view of the molecule with the crystallographic numbering (H atoms omitted).

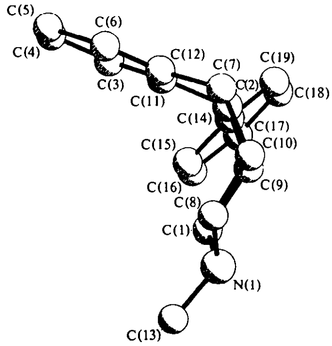
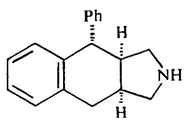


Fig. 2. A view nearly along the C(2)–C(7) bend axis of the molecule, showing the L shape.

Although *R* is somewhat high, probably because of the poor crystal quality, the constitution and conformation are not in doubt. Apart from the phenyl substituent, the molecule has almost perfect mirror symmetry (Fig. 1). The molecule is bent along the middle [C(2)–C(7)] of the cyclohexane ring, which thus has a boat conformation. The phenyl group is at the prow and equatorial, which is the least hindered arrangement and is rotated so that its plane is roughly coincident with the C(2)–C(7) local mirror plane of the cyclohexane ring. The five-membered ring has an envelope conformation with N(1) at the flap. The methyl group is pseudo equatorial so that the lone pair is pointing away from the aromatic ring (although this whole system is almost certainly conformationally mobile in solution). The conformation of the five-membered ring and its methyl substituent mean that the molecule has a rather flat end so that it is essentially L-shaped (Fig. 2).

The structure of a similar molecule (III) has been reported (Oppolzer, Achini, Pfenninger & Weber, 1976) in which the configuration of the phenyl substituent is α. Again, the phenyl group is found to be equatorial but because of the different configuration the bend along C(2)–C(7) is in the opposite direction. This results in the tricyclic system being much flatter. It seems that in both (II) and (III) the steric bulk of the phenyl group determines the conformation of the cyclohexane ring and hence the shape of the molecule.



(III)

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Structure of the 1:1 complex of Trithia(5)heterohelicene* and 7,7,8,8-Tetracyano-*p*-quinodimethane

By M. Konno, Y. Saito, K. Yamada† and H. Kawazura†

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

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Abstract. $C_{16}H_8S_3.C_{12}H_4N_4$, $M_r = 500{\cdot}6$, $C2/c$, $a = 21{\cdot}478$ (4), $b = 8{\cdot}548$ (3), $c = 13{\cdot}841$ (3) Å, $\beta = 114{\cdot}86$ (2)°, $U = 2305{\cdot}7$ (7) Å^3, $D_m = 1{\cdot}448$, $D_x = 1{\cdot}442$ Mg m^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 0·341 mm^{-1}. The structure was refined to an R value of 0·048 for 1543 observed reflections collected by X-ray diffractometry. Heterohelicene and TCNQ molecules are stacked alternately in infinite columns along **c**. The heterohelicene molecule is overcrowded. The bending between adjacent rings relieves the repulsion between H(8) and H(8′). Thus the molecule has a helical structure, the terminal five-membered rings being inclined at an angle of 29·6° to each other.

Introduction. Attention has been paid to the hexahelicene molecule as an inherently dissymmetric chromophore (Newman & Lednicer, 1956; Moscowitz, 1961). The CD and ORD spectra of heterohelicene molecules were quite different from those of the hexahelicene molecule (Groen & Wynberg, 1971). The present investigation was undertaken to throw some light on this phenomenon and to study the charge-transfer interaction between TCNQ and heterohelicene molecules. Crystals are greenish-black needles. Preliminary oscillation and Weissenberg photographs depicted a monoclinic lattice with systematic absences hkl with $h + k$ odd and $h0l$ with h, l odd, consistent with space groups $C2/c$ and Cc. A successful structure analysis was accomplished in $C2/c$. Intensity data were collected on an automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The intensities of reflections with $2\theta \leq 55°$ were measured by means of the 2θ–ω scan technique. 1543 independent reflections with $|F| \geq 3\sigma$ were collected. Lorentz and polarization corrections were applied but no correction for absorption was made.

Sharpened Patterson maps gave the positions of three S atoms. Fourier maps phased by these atoms revealed the non-hydrogen atoms. After several refinements by block-diagonal least-squares methods, all the H atoms could be located. The final refinement was carried out by the full-matrix least-squares program *RADIEL* (Yang, Becker & Coppens, unpublished) with anisotropic temperature factors for non-hydrogen atoms and isotropic for H. The final R value was 0·048. The scattering factors of Stewart, Davidson & Simpson (1965) were used for H atoms and all other scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameter shifts were all less than one tenth of the corresponding standard deviations. Final atomic parameters are listed in Table 1.‡

Discussion. Thermal ellipsoids of the non-hydrogen atoms of a heterohelicene molecule are shown in Fig. 1. The heterohelicene molecule possesses a crystallographic C_2 axis passing through the central S atom and the center of the C(14)–C(14′) bond. A planar configuration through the entire molecule is expected, owing to the conjugation of double and single bonds; however, the steric repulsion between the two terminal

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[*] IUPAC name: thieno[3,2-e:4,5-e']bis(benzo[b]thiophene).

[†] Present address: Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02, Japan.

[‡] Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35159 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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