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Structure of Methyl 8-Methyl-1,3-diphenyl-3a,8,9,9a-tetrahydrobenzo[*e*]indazole-9a-carboxylate

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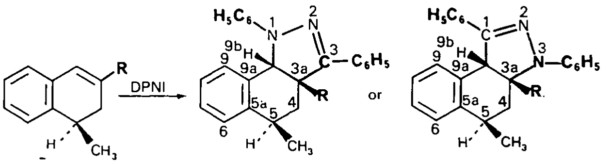
Abstract. $C_{26}H_{24}N_2O_2$, $M_r = 396{\cdot}5$, monoclinic, $C2/c$, $a = 29{\cdot}363\,(3)$, $b = 8{\cdot}143\,(1)$, $c = 17{\cdot}442\,(2)$ Å, $\beta = 93{\cdot}07\,(1)°$, $V = 4164$ Å^3, $Z = 8$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\bar{\lambda}(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}56$ mm^{-1}, $R = 0{\cdot}042$, $wR = 0{\cdot}048$ for 2147 independent observed reflections. The diastereoisomeric *trans* configuration is clearly revealed. The pyrazolinic ring is formed by regioselective 1,3-dipolar cycloaddition [$\mathrm{C{=}N} = 1{\cdot}293\,(3)$, $\mathrm{N{-}N} = 1{\cdot}367\,(3)$ Å]. The cyclohexenic moiety of the cycloadduct has a half-boat conformation.

Introduction. In a previous work (Tshiamala, Vebrel & Laude, 1985), we have shown that ^{1}H NMR data can specify the stereochemistry of the major cycloadduct (2) ($R = \mathrm{H}$) provided by the reaction of diphenylnitrilimine (DPNI) towards 1-methyl-1,2-dihydronaphthalene (1) ($R = \mathrm{H}$). The isolated cycloadduct (2) ($R = \mathrm{H}$) presents a *trans* configuration for the 5-methyl group and the pyrazolinic ring created by 1,3-dipolar cycloaddition. The regiochemistry has already been revealed by Huisgen, Seidel, Wallbillich & Knupfer (1962).



(1) (2) (3)

We wished to study the influence of the ester group ($R = \mathrm{CO_2Me}$) on the regio- and stereochemistry of the reaction of the same 1,3-dipole (DPNI) on the methyl 1-methyl-1,2-dihydronaphthalene-3-carboxylate (1) ($R = \mathrm{CO_2Me}$). ^{1}H NMR spectroscopic data allow us to determine the stereochemistry of the single isolated cycloadduct: the approach of the dipole occurs also from the less-hindered diastereotopic side of the dipolarophile (1), *i.e.* *anti* to the 1-methyl group.

However, these NMR data do not ascertain the

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regiochemistry of the cycloaddition. Indeed, the chemical-shift values of the H(9b) proton of each cycloadduct are the same $\{R = \mathrm{H},\ \delta[\mathrm{H(9b)}] = 5{\cdot}12;\ R = \mathrm{CO_2Me},\ \delta[\mathrm{H(9b)}] = 5{\cdot}15\}$. One could even think that these very close values support the same regiochemistry for the two cycloaddition reactions.

The present determination of the structure of the cycloadduct obtained from (1) ($R = \mathrm{CO_2Me}$) shows the reverse and the regioisomer (3) ($R = \mathrm{CO_2Me}$) is retained. The other data allow us to verify the stereochemistry and also to determine the conformation of the cycloadduct.

Experimental. Colourless prisms of the title compound were obtained by recrystallization from ethanol. Crystal size $0{\cdot}12 \times 0{\cdot}20 \times 0{\cdot}10$ mm. 3617 intensities (with hkl: $h + k = 2n$) recorded on a Nonius CAD-4 diffractometer at the Centre de Diffractométrie Automatique de Lyon. Monochromated Cu $K\alpha$ radiation, $2\theta_{\max}$ 124°. No significant intensity change of the check reflection. R_{int} 0·021 for 3270 unique reflections (index ranges after merging: h −32→32, k 0→9, l 0→19), 2147 data with $F > 5\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1981). Cell constants refined from 25 reflections with $30 < 2\theta < 40°$. No absorption correction.

Structure solution by routine direct methods in centrosymmetric space group $C2/c$. Distinction between C(1) and N(3) atoms (each bearing a phenyl group) was unambiguously deduced from isotropic thermal parameters and bond lengths in the initial refinement in which both were assigned as C.

Refinement on F to R 0·042, wR 0·048 [all non-H atoms anisotropic; H atoms included using riding model with C—H 0·96 Å; $U(\mathrm{H}) = 0{\cdot}075$ Å^2 for aromatic, C—H and CH$_2$ atoms, $U(\mathrm{H}) = 0{\cdot}100$ Å^2 for the methyl H atoms]; 287 parameters; weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0002F^2$; $S = 1{\cdot}45$; $(\Delta/\sigma)_{\max} = 0{\cdot}2$. Maximum and minimum heights in final $\Delta\rho$ map $+0{\cdot}15$ and $-0{\cdot}21$ e Å^{-3}. Atomic scattering factors as incorporated in *SHELXTL*.

Discussion. Final atomic coordinates are given in Table 1* with derived parameters in Table 2. The *ORTEP* view (Johnson, 1976) of the molecule (Fig. 1) displays the atom labelling and the main conformational features. Only four H atoms have been shown to illustrate the relative configurations.

The R group (methoxycarbonyl) lies in an axial configuration whereas the methyl group C(51) and H(9b) are equatorial: angles of 10·6 and 10·3°

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^4)

$$U_{\mathrm{eq}} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
C(9a)	3219 (1)	3103 (3)	1424 (1)	518 (15)
C(5a)	2877 (1)	2046 (3)	1124 (1)	572 (16)
C(6)	2423 (1)	2542 (4)	1126 (2)	767 (21)
C(7)	2306 (1)	4036 (3)	1433 (2)	906 (26)
C(8)	2640 (1)	5055 (4)	1742 (2)	876 (24)
C(9)	3099 (1)	4602 (3)	1739 (1)	672 (19)
C(9b)	3709 (1)	2578 (3)	1401 (1)	480 (13)
C(3a)	3787 (1)	754 (3)	1660 (1)	471 (14)
C(4)	3353 (1)	−298 (3)	1534 (1)	571 (16)
C(5)	3030 (1)	361 (3)	880 (2)	598 (17)
C(31)	4372 (1)	−1264 (3)	1141 (1)	504 (14)
C(32)	4336 (1)	−2366 (3)	1746 (1)	584 (17)
C(33)	4584 (1)	−3818 (4)	1750 (2)	693 (19)
C(34)	4865 (1)	−4164 (4)	1166 (2)	834 (23)
C(35)	4899 (1)	−3068 (4)	570 (2)	779 (21)
C(36)	4655 (1)	−1643 (3)	553 (2)	611 (17)
C(11)	3817 (1)	3701 (3)	−12 (1)	534 (14)
C(12)	3830 (1)	3161 (4)	−767 (1)	690 (17)
C(13)	3740 (1)	4141 (5)	−1364 (2)	839 (22)
C(14)	3641 (1)	5851 (5)	−1223 (2)	835 (22)
C(15)	3633 (1)	6403 (4)	−483 (2)	791 (20)
C(16)	3717 (1)	5336 (3)	127 (2)	663 (17)
C(1)	3900 (1)	2519 (3)	611 (1)	486 (13)
C(30)	3965 (1)	717 (3)	2491 (1)	509 (13)
C(40)	4600 (1)	1225 (4)	3349 (1)	824 (20)
C(51)	2641 (1)	−843 (4)	703 (2)	873 (21)
O(1)	3757 (1)	228 (2)	3013 (1)	738 (12)
O(2)	4385 (1)	1324 (2)	2578 (1)	649 (11)
N(3)	4140 (1)	248 (2)	1138 (1)	584 (12)
N(2)	4150 (1)	1240 (3)	507 (1)	563 (12)

Table 2. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and dihedral angles* (°)

C(9a)–C(5a)	1·402 (4)	C(11)–C(12)	1·391 (3)	C(31)–C(32)	1·395 (4)
C(5a)–C(6)	1·391 (4)	C(12)–C(13)	1·383 (4)	C(32)–C(33)	1·388 (4)
C(6)–C(7)	1·380 (5)	C(13)–C(14)	1·369 (5)	C(33)–C(34)	1·376 (5)
C(7)–C(8)	1·372 (5)	C(14)–C(15)	1·369 (4)	C(34)–C(35)	1·377 (5)
C(8)–C(9)	1·396 (5)	C(15)–C(16)	1·386 (4)	C(35)–C(36)	1·365 (4)
C(9)–C(9a)	1·391 (4)	C(16)–C(11)	1·388 (4)	C(36)–C(31)	1·388 (4)
Mean	1·389	Mean	1·380	Mean	1·381

C(5a)–C(5)	1·513 (4)	C(9b)–C(1)	1·516 (3)	C(5)–C(51)	1·523 (4)
C(5)–C(4)	1·540 (4)	C(1)–N(2)	1·293 (3)	C(3a)–C(30)	1·514 (3)
C(4)–C(3a)	1·542 (3)	N(2)–N(3)	1·367 (3)	C(30)–O(1)	1·193 (3)
C(3a)–C(9b)	1·566 (3)	N(3)–C(3a)	1·473 (3)	C(30)–O(2)	1·330 (3)
C(9b)–C(9a)	1·505 (4)	C(1)–C(11)	1·462 (3)	O(2)–C(40)	1·457 (3)
C(9b)–C(3a)	1·566 (3)	N(3)–C(31)	1·407 (3)		

C(9b)–C(9a)–C(5a)	118·9 (2)	C(1)–C(9b)–C(3a)	100·1 (2)
C(9a)–C(5a)–C(5)	116·3 (2)	C(9b)–C(3a)–N(3)	100·6 (2)
C(5a)–C(5)–C(4)	106·8 (2)	C(3a)–N(3)–N(2)	112·2 (2)
C(5)–C(4)–C(3a)	112·5 (2)	N(3)–N(2)–C(1)	109·0 (2)
C(4)–C(3a)–C(9b)	112·3 (2)	N(2)–C(1)–C(9b)	113·2 (2)
C(3a)–C(9b)–C(9a)	112·8 (2)		

C(3a)–N(3)–C(31)	126·9 (2)	N(3)–C(31)–C(32)	120·6 (2)
N(2)–N(3)–C(31)	119·2 (2)	N(3)–C(31)–C(36)	120·1 (2)
C(9b)–C(1)–C(11)	126·9 (2)	C(1)–C(11)–C(16)	122·0 (2)
N(2)–C(1)–C(11)	119·9 (2)	C(1)–C(11)–C(12)	118·9 (2)

C(4)–C(3a)–N(3)	111·1 (2)	C(3a)–C(30)–O(1)	125·1 (2)
C(4)–C(3a)–C(30)	111·4 (2)	C(3a)–C(30)–O(2)	111·8 (2)
C(9b)–C(3a)–C(30)	109·4 (2)	O(1)–C(30)–O(2)	123·1 (2)
		C(30)–O(2)–C(40)	116·0 (2)

C(6)–C(5a)–C(5)–C(51)	5·6 (4)	C(9)–C(9a)–C(9b)–H(9b)	10·7 (6)
C(9)–C(9a)–C(9b)–C(1)	110·8 (4)		

Mean plane (1): |C(5a)–C(9a)–C(9)–C(8)–C(7)–C(6)| planar to within 0·01 Å
Mean plane (2): |C(11)–C(12)–C(13)–C(14)–C(15)–C(16)| planar to within 0·02 Å
Mean plane (3): |C(31)–C(32)–C(33)–C(34)–C(35)–C(36)| planar to within 0·01 Å
Mean plane (4): |C(3a)–N(3)–N(2)–C(1)–C(9b)| planar to within 0·13 Å
Mean plane (5): |C(3a)–C(30)–O(1)–O(2)–C(40)| planar to within 0·04 Å

Angles between the mean planes

(1)–(2)	77·4 (1)	(1)–(3)	80·4 (1)	(1)–(4)	79·8 (1)
(1)–(5)	77·6 (1)	(2)–(3)	54·5 (1)	(2)–(4)	33·6 (1)
(2)–(5)	81·6 (1)	(3)–(4)	3·2 (1)	(3)–(5)	76·4 (1)

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44330 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

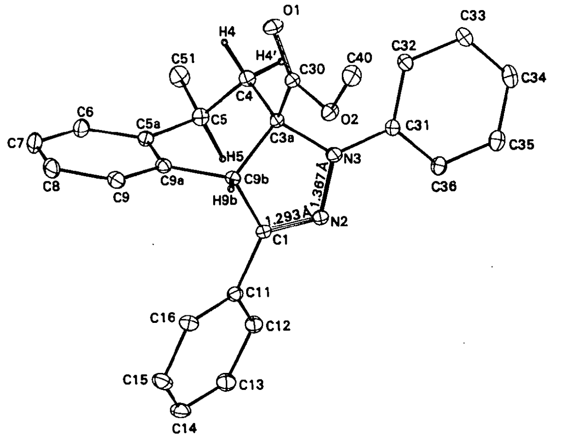

Fig. 1. Perspective view of the molecule with atom labelling.

respectively *versus* the benzo ring (plane 1). The regioisomer (3) is clearly revealed. The cyclohexenic ring has a half-boat conformation [C(4) 1·31 Å above the benzo ring], the C(5) atom being slightly displaced (0·16 Å) in the same way as in a similar previously studied compound (Mercier, Kitane, Tshiamala, Vebrel, Laude & Sheldrick, 1986).

The C—C bond common to the five- and six-membered rings (1·566 Å) is comparable to analogous bonds observed in fused pentagonal rings (Mercier, Ramah, Laude, Faure & Loiseleur, 1984). The C=N double bond is not conjugated with the α-phenyl group (plane 2) (angle 22·3° with plane 2) but is exactly coplanar with the β-phenyl group (plane 3) as is the pyrazolinic plane.

The regioisomer (3) is clearly revealed by the typical bond lengths of the C=N—N group [C=N = 1·293, N(2)—N(3) = 1·367 Å] as well as the C(3a)—N(3) = 1·473 Å and C(9b)—C(1) = 1·516 Å bonds of the pyrazolinic ring.

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Quinol–1,8-Epoxymenthane (1/2)*

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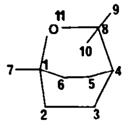
Abstract. $C_6H_6O_2.2C_{10}H_{18}O$, $M_r = 418{\cdot}62$, monoclinic, $P2_1/n$, $a = 7{\cdot}6793\ (3)$, $b = 15{\cdot}1204\ (8)$, $c = 10{\cdot}8318\ (13)$ Å, $\beta = 102{\cdot}260\ (7)°$, $V = 1229{\cdot}04$ Å^3, $Z = 2$, $D_x = 1{\cdot}13$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}51$ cm^{-1}, $F(000) = 460$, $T = 293$ K, $R = 0{\cdot}046$ for 1870 reflexions. The complex occurs as isolated trimolecular units with O···H—O bonding [2·724 (2) Å]. The torsion angle about the O···H link [32·3 (5)°] implies partial involvement of both lone pairs of electrons of the ether O atom. Other bond lengths and angles have typical values.

Introduction. 1,8-Epoxymenthane (1,8-cineole), CIN, is a cyclic ether where, in spite of the bulk of the molecule, the lone pairs of electrons on the oxygen atom are well exposed to the approach of other species. Thus CIN can act as a monodentate ligand in complexes such as $SnCl_4.2CIN$ (Sumarova & Nevskaya, 1956).



CIN

Attempts in our laboratory to investigate the crystal structures of the complexes of CIN with iodine, silver perchlorate, tin(II) bromide and ferric chloride have been abandoned because of inadequate crystal quality and low thermal stability. An alternative role for CIN is in the formation of hydrogen-bonded complexes similar to those formed by the bridging cyclic diether 1,4-

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* Quinol is 1,4-benzenediol.

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