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Racemic 3-Methyl-*r*-2,*c*-3,*c*-5-triphenylpyrrolidine and 3-Methyl-*r*-2,*t*-3,*c*-5-triphenylpyrrolidine

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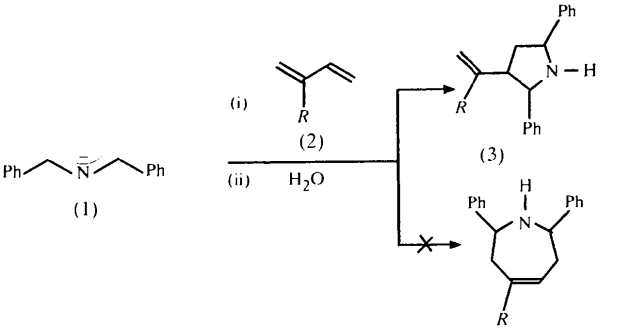
Abstract

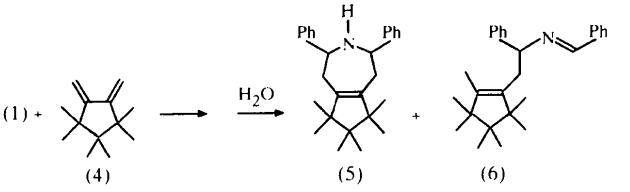
The 1,3-diphenyl-2-azaallyl anion adds almost quantitatively to 2-phenylpropene with retention of the conformation of the anion. Two racemic diastereoisomeric [3+2] cycloadducts, *i.e.* the corresponding pyrrolidines, are formed, in which both phenyl substituents derived from the anion are *cis* oriented. The structures of racemic 3-methyl-*r*-2,*c*-3,*c*-5-triphenylpyrrolidine, $C_{23}H_{23}N$, (I), and 3-methyl-*r*-2,*t*-3,*c*-5-triphenylpyrrolidine, $C_{23}H_{23}N$, (II), were determined by X-ray analysis. There is no intermolecular hydrogen bonding in either crystal.

Comment

The 1,3-diphenyl-2-azaallyl anion, (1), adds stereospecifically to *E*/*Z*-isomeric alkenes with retention of the configuration of the alkene and the conformation of the azaallyl anion (Kauffmann & Köppelmann, 1972). This result is in accord with a concerted process (Woodward & Hoffmann, 1969), where the anion behaves as a $_{\pi}4s$ cycloaddition partner. The mechanistic significance of this observation has been questioned (Huisgen, 1984), however, because the isolated yields of the cycloadducts were rather low. The exclusive formation (Scheme 1) of a single 3-vinylpyrrolidine, (3), in the reaction of this anion with 1,3-dienes, (2) (Kauffmann & Eidenschink, 1971), would be additional evidence for a concerted cycloaddition, but quite recently, [4+3]-cycloaddition and 1,4-addition products [(5) and (6), respectively] were found to be formed in moderate yields when the 1,3-diphenyl-2-azaallyl anion, (1), was combined with 3,3,4,4,5,5-hexamethyl-1,2-bis(methylene)cyclopentane, (4) (Mayr *et al.*, 1993) (Scheme 2). Both reaction partners showed $_{\pi}4$ reactivity resulting in the formation of a seven-membered ring. This last result can only be rationalized by a stepwise $_{\pi}4 + _{\pi}4$ cycloaddition process. A similar rather unusual result has been obtained for the reaction of the diene (4) with *C*,*N*-diphenylnitrone (Baran & Mayr, 1987). The sterically encumbered double bond and the allylic stabilization of the intermediate would be two reasons for the stepwise mechanism operating in these cases (Baran & Mayr, 1989; Mayr *et al.*, 1991).



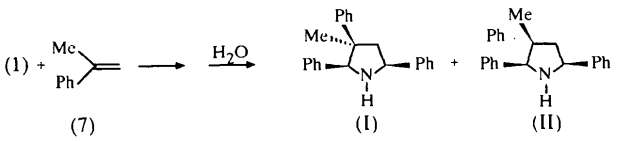
Scheme 1



Scheme 2

Similar factors can operate in the reaction of the anion (1) with 2-phenylpropene, (7), which was investigated next (Scheme 3). The reaction is almost quantitative and results in the formation of only two diastereoisomers of the [3+2] cycloadducts, (I) and (II), the structures

of which were tentatively assigned as being derived from the 'W' form of anion (1) (Kauffmann *et al.*, 1972; Young & Ahmad, 1982). The reaction products were thoroughly checked by NMR, GC/MS and HPLC, but no evidence of other isomers derived from the two other forms of anion (1) or rotamers of the possible intermediates have been found.



Scheme 3

The structure determinations of the title compounds, (I) and (II), were undertaken in order to obtain an unequivocal picture of the substitution processes in the pyrrolidine ring, and to prove the conservation of the configuration of the 1,3-dipole during this cycloaddition.

The title isomers (I) and (II) (Figs. 1 and 3, respectively) differ only in the relative configuration of the phenyl and methyl substituents at C3. The crystal of (II) is built up of two crystallographically independent molecules, *A* and *B*, which have similar geometrical parameters (within the limits of four s.u.'s). Molecule *A* is closely related to the enantiomer of molecule *B* by a pseudo-center of inversion. Fig. 2 illustrates these molecules, with the non-H atoms of the two molecules fitted.

The five-membered rings of (I) and (II) each have a distorted envelope conformation with the N atom on the flap. It is worth noting that, in the five-membered ring of (I), there is a long C2—C3 bond distance of 1.587 (3) Å, and a contracted C2—C3—C4 bond angle of 101.6 (2)°. These structural features result from the arrangement of the bulky substituents at C3. Similar (even larger) deformation effects for a small ring with bulky substituents have been observed in

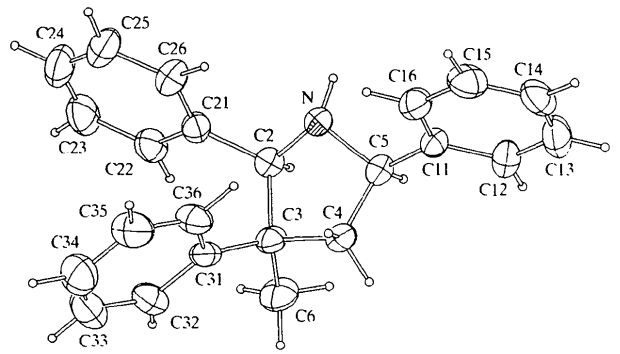


Fig. 1. The molecular structure and numbering scheme of (I). Displacement ellipsoids are shown at the 50% probability level.

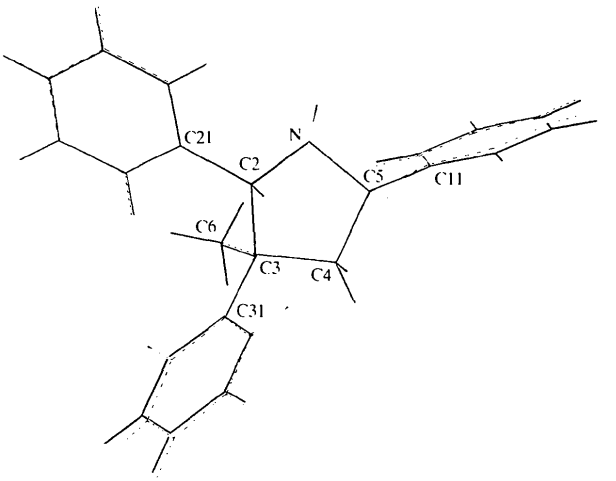


Fig. 2. A view of the two molecules, *A* and *B*, of (II), with the non-H atoms of the two molecules superimposed (molecule *B* as dashed lines).

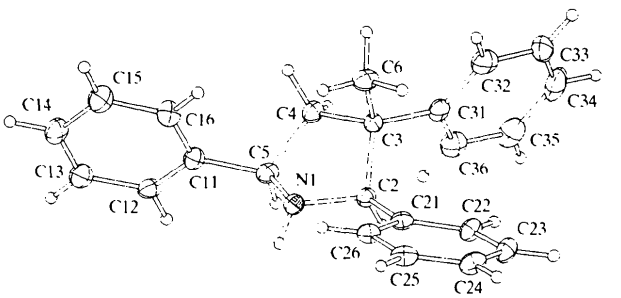


Fig. 3. The molecular structure and numbering scheme of (II), molecule *A*. Displacement ellipsoids are shown at the 50% probability level.

1,2,2,3,3,4,4,5-octamethyl-6,7,8-trioxabicyclo[3.2.1]-octane (Jerzykiewicz *et al.*, 1993). The other C—C as well as the N—C bond lengths are in reasonable agreement with values reported for many compounds with a pyrrolidine system (Bachechi *et al.*, 1980; Ried *et al.*, 1981; Aubé *et al.*, 1992). Neither structure shows any evidence of intermolecular hydrogen bonding.

Experimental

IR spectra were recorded on a Shimadzu IR-435 spectrometer. NMR spectra (200 MHz) were taken on a Varian XL 200 spectrometer by using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. Mass spectra (EI) were recorded on a 70–250E VG spectrometer. Melting points are uncorrected. The preparative MPLC separations were carried out on 30 × 2.5 cm columns filled with LiChroprep (RP-18, 15–20 μ particles). The reaction was performed in an oven-dried flask under nitrogen at room temperature. Diisopropylamine (1.24 g, 12.4 mmol) in 5 ml of tetrahydrofuran (THF) was added to a 1.6 *M* solution of butyllithium in hexane (7.1 ml, 11.3 mmol). The lithium diisopropylamide solution thus obtained was

stirred for a few minutes and after the addition (2 min) of *N*-benzylidenebenzylamine (2.0 g, 10.25 mmol) in THF (5 ml), the deep-purple–red solution of (1) was stirred for 0.5 h. 2-Phenylpropene, (7) (1.21 g, 10.25 mmol), in 5 ml of THF was subsequently added and the reaction mixture was stirred at ambient temperature for 0.5 h. Water was then added and the mixture extracted with five 20 ml portions of ether. The combined ether extracts were dried with sodium carbonate and after removal of the solvents under reduced pressure, a few drops of methanol were added to the yellowish residue. The precipitate was collected by filtration and washed with cold methanol to give a colorless product (3.15 g; 98%). Pure isomers were isolated by preparative MPLC (MeOH:H_2O 80:20) and recrystallized from methanol. Minor isomer, (I). M.p. 388–389 K. IR (KBr): ν = 3415 cm^{-1} (broad N—H). ^1H NMR (200 MHz; $CDCl_3$), δ (p.p.m.): 1.69 (*s*, 3H), 2.15 (broad, NH, 1H), *ABX* system with ν_A = 2.41, ν_B = 2.52, ν_X = 4.58 and J_{AB} = 13.0 Hz, J_{AX} = 8.15 Hz, J_{BX} = 9.15 Hz (3H), 4.30 (*s*, 1H), 6.91–7.66 (*m*, 15H, aromatic H). ^{13}C NMR (50 MHz; $CDCl_3$), δ (p.p.m.): 28.21 (*q*), 50.00 (*s*), 50.10 (*t*), 59.74 (*d*), 74.46 (*d*), 125.27, 126.28, 126.31, 126.53, 126.60, 126.91, 127.09, 127.27, 127.45, 127.61, 127.66, 128.46 (12 *d*), 141.34, 144.27, 146.24 (3 *s*). MS (70 eV), *m/z* (%): 313 (0.8) [M^+], 196 (15), 195 (100), 194 (52), 193 (15), 115 (13), 91 (20), 90 (11), 89 (12), 77 (14), 40 (12). $C_{23}H_{23}N$ requires 313.18305, found 313.18180 (MS). Major isomer, (II). M.p. 351–352 K. IR (KBr): ν = 3411 cm^{-1} (broad N—H). ^1H NMR (200 MHz; $CDCl_3$), δ (p.p.m.) 1.10 (*s*, 3H), 2.20 (broad NH, 1H), *ABX* system with ν_A = 1.97, ν_B = 2.83, ν_X = 4.65 and J_{AB} = 12.85 Hz, J_{AX} = 9.2 Hz, J_{BX} = 8.15 Hz (3H), 4.60 (*s*, 1H), 7.10–7.64 (*m*, 15H, aromatic H). ^{13}C NMR (50 MHz; $CDCl_3$): δ (p.p.m.) 23.87 (*q*), 48.56 (*s*), 52.60 (*t*), 60.82 (*d*), 74.45 (*d*), 125.82, 126.73, 126.90, 127.24, 127.57, 128.12, 128.38 (7 *d*), 140.29, 145.01, 148.57 (3 *s*). MS (70 eV), *m/z* (%): 313 (0.4) [M^+], 196 (15), 195 (100), 194 (50), 193 (13), 116 (10), 115 (10), 91 (19), 90 (10), 89 (10), 77 (12). $C_{23}H_{23}N$ requires 313.18305, found 313.18832 (MS).

Compound (I)

Crystal data

$C_{23}H_{23}N$
M_r = 313.42
Orthorhombic
Pbca
a = 8.514 (6) Å
b = 19.390 (12) Å
c = 21.940 (12) Å
V = 3622 (4) Å^3
Z = 8
D_x = 1.150 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 7–11°
μ = 0.066 mm^{-1}
T = 301 (2) K
Plate
0.7 × 0.6 × 0.2 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
5045 measured reflections
3141 independent reflections
1429 reflections with $I > 2\sigma(I)$

R_{int} = 0.068
θ_{max} = 26°
$h = -7 \rightarrow 10$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 27$
3 standard reflections
every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.026
3141 reflections
309 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.050
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{23}H_{23}N$
M_r = 313.42
Orthorhombic
$Pca2_1$
a = 24.52 (2) Å
b = 6.369 (6) Å
c = 22.40 (2) Å
V = 3498 (6) Å^3
Z = 8
D_x = 1.190 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 67 reflections
θ = 9–13°
μ = 0.068 mm^{-1}
T = 100 (2) K
Needle
0.8 × 0.3 × 0.2 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
4391 measured reflections
4391 independent reflections
2899 reflections with $I > 2\sigma(I)$

θ_{max} = 32.5°
$h = 0 \rightarrow 36$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 33$
3 standard reflections
every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.154
S = 1.012
4391 reflections
438 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.088P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.036
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) of the title compounds*

	(I)	(IIA)	(IIB)
N—C2	1.454 (3)	1.487 (5)	1.459 (5)
N—C5	1.470 (3)	1.477 (5)	1.493 (5)
C5—C11	1.490 (3)	1.502 (6)	1.498 (6)
C2—C21	1.504 (3)	1.520 (5)	1.510 (5)
C3—C31	1.512 (3)	1.523 (6)	1.534 (6)
C2—C3	1.587 (3)	1.560 (6)	1.560 (5)
C3—C4	1.550 (3)	1.562 (6)	1.544 (6)
C3—C6	1.528 (4)	1.537 (5)	1.526 (6)
C4—C5	1.516 (4)	1.547 (6)	1.548 (6)
C2—N—C5	104.4 (2)	103.6 (3)	105.2 (3)
N—C2—C3	103.5 (2)	101.5 (3)	101.7 (3)
N—C5—C4	100.1 (2)	102.7 (3)	101.7 (3)
N—C5—C11	113.9 (2)	112.5 (3)	112.7 (3)
N—C2—C21	112.9 (2)	113.1 (3)	113.0 (3)

C2—C3—C4	101.6 (2)	101.6 (3)	101.8 (3)
C2—C3—C6	108.1 (3)	109.9 (3)	109.6 (3)
C3—C4—C5	106.1 (2)	106.4 (3)	107.2 (3)
C4—C3—C6	109.4 (2)	108.1 (3)	109.6 (3)
C11—C5—C4	115.6 (2)	114.7 (3)	115.6 (3)
C21—C2—C3	116.5 (2)	115.5 (3)	116.2 (3)
C31—C3—C6	112.5 (2)	113.9 (3)	112.8 (3)
C31—C3—C4	113.2 (2)	112.2 (3)	111.3 (3)
C31—C3—C2	111.4 (2)	110.5 (3)	111.1 (3)

The structure analysis of (I) proceeded routinely and the H atoms were located by difference syntheses and refined isotropically. For (II), systematic absences indicated the possible space groups $Pca2_1$ or *Pcam*. A satisfactory solution was obtained in the non-centrosymmetric space group with two molecules in the asymmetric unit. The C-bonded H atoms were included in geometrically calculated positions and N-bonded H atoms were found from difference Fourier maps and refined isotropically. The collection of data at low temperature was carried out in order to improve the counting statistics [using an Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986)]. In the case of (II), the absolute direction of the polar axis cannot be determined reliably since the values of anomalous dispersion for the heaviest O atoms in the case of molybdenum radiation are very small.

For both compounds, data collection: *Kuma KM-4 Software* (Kuma Diffraction, 1989); cell refinement: *Kuma KM-4 Software*; data reduction: *Kuma KM-4 Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1033). Services for accessing these data are described at the back of the journal.

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Ethyl 3,5-Dimethyl-4-oxo-*cis*-2,6-diphenylpiperidine-1-carboxylate

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Abstract

The piperidine ring in the title compound, $C_{22}H_{25}NO_3$, adopts a distorted-boat conformation. Some conjugation of the lone pair of the N atom with the carbonyl group is observed. The two phenyl rings form dihedral angles of 88.9 (1) and 79.1 (1)° with the best plane through the piperidine ring.

Comment

Piperidine derivatives are used clinically to prevent post-operative vomiting, to speed up gastric emptying before anaesthesia or to facilitate radiological evaluation, and to correct a variety of disturbances of gastrointestinal functions (Robinson, 1973). Several 2,6-disubstituted piperidines are found to be useful as tranquilisers (Bochringer & Soehne, 1961) and possess hypotensive activity (Severs *et al.*, 1965), and a combination of stimulant and depressant effects on the central nervous system (Ganellin & Spickett, 1965), as well as bactericidal, fungicidal and herbicidal activities (Mobio *et al.*, 1990).

The torsion angles of the title compound, (I), show that the piperidine ring adopts a distorted-boat conformation. The carbonyl group of the ethoxycarbonyl moiety shows some conjugation with the N1 atom of the piperidine ring; N1—C19 1.367 (3) and C19—O20 1.204 (3) Å, the N1 atom being 0.156 (2) Å out of the C2, C6, C19 plane. The methyl groups in the 3 and 5 positions of the piperidine ring assume axial and equatorial