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Structure of 3,4-Dihydro-3-methyl-1′-phenyl-3′,4′-di-*p*-tolylspiro[naphthalene-2,5′-[2]pyrazoline]-1(2*H*)one

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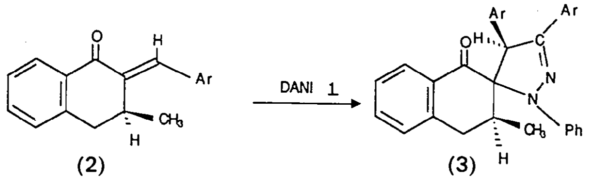
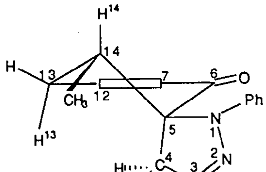
Abstract. $C_{33}H_{30}N_2O$, $M_r = 470{\cdot}6$, orthorhombic, *Pbca*, $a = 10{\cdot}199$ (3), $b = 15{\cdot}518$ (3), $c = 32{\cdot}625$ (8) Å, $V = 5163$ (4) Å^3, $Z = 8$, $D_x = 1{\cdot}211$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}0679$ mm^{-1}, $F(000) = 2000$, $T = 293$ K, $R = 0{\cdot}053$ for 1313 unique reflections. The conformation of the title compound shows that the approach of the dipole (diarylnitrilimine) occurs towards the less hindered side of the dipolarophile. Furthermore the ketonic ring of the cycloadduct is in a 1,3-diplanar conformation.

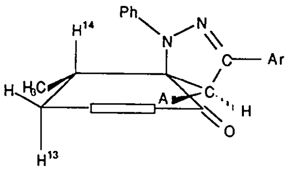
Introduction. In a previous work (Kerbal, Tshiamala, Vebrel & Laude, 1988) on the cycloaddition of diarylnitrilimines [DANI, (1)] to 2-arylidene-1-indanones, the diastereochemistry of the dipole–dipolarophile approach has been studied. We wished to extend this investigation to the behaviour of more pliable dipolarophiles, *i.e.* the 3-methyl-2-arylidene-1-tetralones (2). NMR (^{1}H, ^{13}C) results threw some light on the regiochemistry of the reaction but gave little information about the stereochemistry of the (sole) cycloaddition product (3). In particular they proved unable to show whether the actual conformation of (3) is (*A*) or (*B*). To solve this ambiguity, the crystal structure of one of the cycloadducts (3) (Ar = *p*-tolyl) is determined in the present paper.



(2) (3)



(*A*)



(*B*)

Experimental. Parallelepiped shaped crystal from an ethanol solution, 0·05 × 0·18 × 0·32 mm. CAD-4 Enraf–Nonius diffractometer, cell parameters determined from 25 reflections having 4·57 ≤ θ ≤

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15·28°. No absorption correction was applied. $\sin\theta/\lambda \le 0{\cdot}504\,\text{Å}^{-1}$, $0 \le h \le 10$, $0 \le k \le 15$, $0 \le l \le 32$; intensity control reflections: $\bar{2}\bar{3}0$, $0,0,\overline{10}$, $0\bar{2}6$; intensity variations during measurements: 1·4%, average $\sigma(I)/I = 0{\cdot}0039$. 2766 unique reflections, 1453 unobserved reflections $[I < \sigma(I)]$. Direct methods, program *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H atoms bonded to C(15), C(16) and C(17) were located from a Fourier difference map. Other H-atom locations were calculated (Frenz, 1982). Atomic diffusion factors were from *International Tables for X-ray Crystallography* (1974). Full-matrix refinements. Refined parameters were x,y,z and β_{ij}'s for C, N and O atoms; H atoms were not refined. For each H atom B was chosen equal to 1 Å^2 + B of the neighbouring heavy atom. $R = 0{\cdot}053$, $wR = 0{\cdot}047$, $w = 1/\sigma^2(F)$, $S = 1{\cdot}24$, maximum shift-to-e.s.d. ratio $(\Delta/\sigma)_{\max} < 0{\cdot}01$, $|\Delta\rho|_{\max} = 0{\cdot}27\,(4)\,\text{e Å}^{-3}$. Program *ORTEP* (Johnson, 1976) was used to represent the molecule (Fig. 1).

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The packing is shown in Fig. 2.

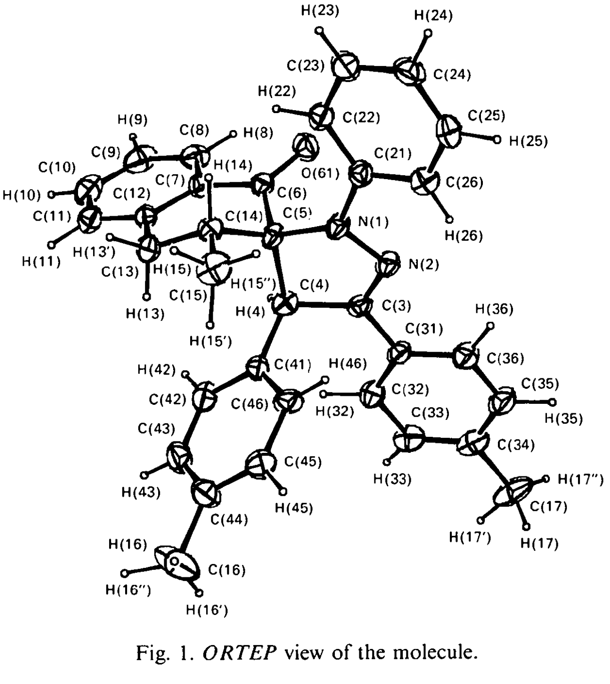

Fig. 1. *ORTEP* view of the molecule.

Table 1. *Positional parameters and their estimated standard deviations*

Ansiotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$.

	x	y	z	B_{eq} (Å^2)
N(1)	0·5132 (4)	0·1664 (3)	0·1397 (1)	3·9 (1)
N(2)	0·5135 (4)	0·1427 (3)	0·0988 (1)	4·0 (1)
C(3)	0·5960 (5)	0·1910 (3)	0·0792 (2)	3·6 (1)
C(4)	0·6617 (5)	0·2588 (3)	0·1057 (2)	3·5 (1)
C(5)	0·6228 (5)	0·2246 (3)	0·1498 (1)	3·5 (1)
C(6)	0·7426 (6)	0·1738 (3)	0·1652 (1)	3·7 (1)
C(7)	0·8568 (5)	0·2253 (3)	0·1793 (1)	3·7 (1)
C(8)	0·9793 (5)	0·1864 (4)	0·1822 (2)	4·7 (1)
C(9)	1·0851 (6)	0·2337 (4)	0·1942 (2)	6·0 (2)
C(10)	1·0699 (6)	0·3196 (4)	0·2034 (2)	6·2 (2)
C(11)	0·9495 (7)	0·3590 (4)	0·2008 (2)	5·4 (2)
C(12)	0·8392 (5)	0·3118 (3)	0·1895 (2)	3·8 (1)
C(13)	0·7074 (6)	0·3538 (3)	0·1880 (2)	4·6 (1)
C(14)	0·5937 (5)	0·2898 (3)	0·1839 (1)	3·8 (1)
C(15)	0·4617 (6)	0·3363 (4)	0·1799 (2)	6·2 (2)
C(16)	0·4957 (9)	0·5993 (4)	0·0507 (3)	10·7 (3)
C(17)	0·6274 (7)	0·1671 (5)	−0·0974 (2)	7·6 (2)
C(21)	0·4326 (5)	0·1169 (3)	0·1655 (2)	3·9 (1)
C(22)	0·4528 (6)	0·1108 (4)	0·2074 (2)	4·6 (1)
C(23)	0·3636 (6)	0·0656 (4)	0·2310 (2)	5·6 (2)
C(24)	0·2565 (7)	0·0258 (4)	0·2147 (2)	5·5 (2)
C(25)	0·2385 (7)	0·0321 (4)	0·1730 (2)	5·9 (2)
C(26)	0·3238 (6)	0·0764 (4)	0·1485 (2)	5·1 (1)
C(31)	0·6104 (5)	0·1832 (3)	0·0347 (1)	3·9 (1)
C(32)	0·6980 (6)	0·2323 (4)	0·0130 (1)	4·5 (1)
C(33)	0·7049 (6)	0·2274 (4)	−0·0297 (2)	5·1 (2)
C(34)	0·6262 (6)	0·1722 (4)	−0·0511 (2)	5·3 (2)
C(35)	0·5404 (6)	0·1206 (4)	−0·0294 (2)	5·8 (2)
C(36)	0·5320 (6)	0·1257 (4)	0·0133 (2)	5·1 (2)
C(41)	0·6180 (5)	0·3471 (3)	0·0920 (1)	3·6 (1)
C(42)	0·7069 (5)	0·4147 (4)	0·0896 (2)	4·9 (2)
C(43)	0·6672 (6)	0·4953 (4)	0·0763 (2)	6·0 (2)
C(44)	0·5398 (7)	0·5107 (4)	0·0648 (2)	5·9 (2)
C(45)	0·4522 (6)	0·4426 (4)	0·0670 (2)	5·5 (2)
C(46)	0·4878 (5)	0·3606 (3)	0·0800 (2)	4·4 (1)
O(61)	0·7461 (4)	0·0950 (2)	0·1641 (1)	4·96 (9)

Mean planes of the different rings

Calculations were made with the *BP7C* program (Ito & Sugawara, 1983). The planarity of the aromatic rings is good. Planes were defined as follows: Π(2) C(21) to C(26) plus N(1), Π(3) C(31) to C(36) plus C(3), Π(4) C(41) to C(46) plus C(4), and Π(5) the aromatic ring of the tetraline C(7) to C(12). The pyrazoline ring Π(1) N(1), N(2), C(3) to C(5), is approximately planar [the maximal distance from the mean plane is 0·129 (4) Å].

The shape of the molecule may be described from four blocks as follows: Π(1) and Π(3) are almost coplanar; the angle between them is less than 1·0 (2)°. Π(2) is approximately parallel to them at an angle of about 18·3 (2)°. Π(4) is approximately perpendicular, Π(1)–Π(4) = 103·9 (2)°, as is the tetralone block, Π(5)–Π(1) = 82·1 (2)°.

Obviously the actual conformation is (*A*). It may be noticed that the conformation of the ketonic ring is indeed of the 1,3-diplanar type. Atoms C(6) and C(13) are almost coplanar with the contiguous benzo ring [mean plane II(5)]. Atoms C(5) and C(14) are on either side of this plane: if the distance from C(5) to Π(5) is taken as +0·495 (11) Å, C(14)–Π(5) = −0·375 (11) Å. These values are incompatible with conformation (*B*).

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* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms, bond distances and angles involving H atoms, and data on average planes of rings have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52669 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°)

N(1)—N(2)	1·382 (5)	C(16)—C(44)	1·518 (9)
N(1)—C(5)	1·475 (6)	C(17)—C(34)	1·513 (7)
N(1)—C(21)	1·406 (6)	C(21)—C(22)	1·384 (7)
N(2)—C(3)	1·297 (6)	C(21)—C(26)	1·391 (8)
C(3)—C(4)	1·517 (7)	C(22)—C(23)	1·383 (8)
C(3)—C(31)	1·465 (7)	C(23)—C(24)	1·363 (9)
C(4)—C(5)	1·583 (7)	C(24)—C(25)	1·377 (8)
C(4)—C(41)	1·507 (7)	C(25)—C(26)	1·367 (8)
C(5)—C(6)	1·538 (7)	C(31)—C(32)	1·370 (8)
C(5)—C(14)	1·534 (7)	C(31)—C(36)	1·386 (8)
C(6)—C(7)	1·487 (8)	C(32)—C(33)	1·397 (7)
C(6)—O(61)	1·223 (6)	C(33)—C(34)	1·366 (8)
C(7)—C(8)	1·391 (8)	C(34)—C(35)	1·382 (8)
C(7)—C(12)	1·393 (7)	C(35)—C(36)	1·396 (7)
C(8)—C(9)	1·364 (8)	C(41)—C(42)	1·389 (8)
C(9)—C(10)	1·374 (9)	C(41)—C(46)	1·401 (7)
C(11)—C(12)	1·393 (8)	C(42)—C(43)	1·384 (8)
C(12)—C(13)	1·496 (8)	C(43)—C(44)	1·373 (9)
C(13)—C(14)	1·532 (8)	C(45)—C(46)	1·390 (8)
C(14)—C(15)	1·533 (8)		

N(2)—N(1)—C(5)	112·1 (4)	C(5)—C(14)—C(15)	114·8 (4)
N(2)—N(1)—C(21)	115·8 (4)	C(13)—C(14)—C(15)	111·5 (4)
C(5)—N(1)—C(21)	130·1 (4)	N(1)—C(21)—C(22)	122·8 (5)
N(1)—C(2)—C(3)	109·0 (4)	N(1)—C(21)—C(26)	118·2 (4)
N(2)—C(3)—C(4)	113·9 (4)	C(22)—C(21)—C(26)	118·9 (5)
N(2)—C(3)—C(31)	120·5 (4)	C(21)—C(22)—C(23)	119·2 (5)
C(4)—C(3)—C(31)	125·3 (4)	C(22)—C(23)—C(24)	122·6 (5)
C(3)—C(4)—C(5)	100·1 (4)	C(23)—C(24)—C(25)	117·5 (6)
C(3)—C(4)—C(41)	109·4 (4)	C(24)—C(25)—C(26)	121·9 (6)
C(5)—C(4)—C(41)	109·4 (4)	C(21)—C(26)—C(25)	120·0 (5)
N(1)—C(5)—C(4)	101·1 (4)	C(21)—C(26)—C(25)	120·0 (5)
N(1)—C(5)—C(6)	111·1 (4)	C(3)—C(31)—C(32)	122·0 (5)
N(1)—C(5)—C(14)	114·8 (4)	C(3)—C(31)—C(36)	119·7 (5)
C(4)—C(5)—C(6)	105·6 (4)	C(32)—C(31)—C(36)	118·3 (5)
C(4)—C(5)—C(14)	119·2 (4)	C(31)—C(32)—C(33)	121·1 (5)
C(6)—C(5)—C(14)	104·8 (4)	C(32)—C(33)—C(34)	121·0 (5)
C(5)—C(6)—C(7)	116·6 (4)	C(17)—C(34)—C(33)	122·6 (5)
C(5)—C(6)—O(61)	121·8 (5)	C(17)—C(34)—C(35)	119·1 (5)
C(7)—C(6)—O(61)	121·5 (5)	C(33)—C(34)—C(35)	118·2 (5)
C(6)—C(7)—C(8)	119·4 (5)	C(34)—C(35)—C(36)	121·1 (6)
C(6)—C(7)—C(12)	119·4 (5)	C(31)—C(36)—C(35)	120·2 (5)
C(8)—C(7)—C(12)	121·2 (5)	C(4)—C(41)—C(42)	120·7 (5)
C(7)—C(8)—C(9)	119·7 (5)	C(4)—C(41)—C(46)	119·9 (5)
C(8)—C(9)—C(10)	119·7 (6)	C(42)—C(41)—C(46)	119·3 (5)
C(9)—C(10)—C(11)	121·3 (6)	C(41)—C(42)—C(43)	120·6 (5)
C(10)—C(11)—C(12)	120·2 (5)	C(42)—C(43)—C(44)	121·3 (6)
C(7)—C(12)—C(11)	117·8 (5)	C(16)—C(44)—C(43)	121·4 (6)
C(7)—C(12)—C(13)	121·9 (5)	C(16)—C(44)—C(45)	121·0 (6)
C(11)—C(12)—C(13)	120·3 (5)	C(43)—C(44)—C(45)	117·6 (5)
C(12)—C(13)—C(14)	113·6 (4)	C(44)—C(45)—C(46)	123·1 (6)
C(5)—C(14)—C(13)	110·2 (4)	C(41)—C(46)—C(45)	118·0 (5)

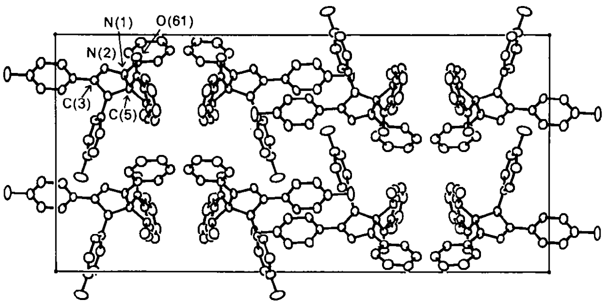

Fig. 2. View of the packing.

Hydrogen atoms H(14) and H(13) are in a trans-pseudodiaxial disposition and situated on either side of Π(5): H(13)–Π(5) = 0·761, H(14)–Π(5) = −1·346 Å. The methyl group linked to C(14) is in a pseudoequatorial position as shown by the torsion angle H(13)—C(13)—C(14)—H(14) = 167·3°. Finally the distance H(4)—O(61) = 3·2 Å is rather large, much too large for a conformation of type (*B*), that would place atoms O(61) and H(4) close to each other, with a distance slightly larger than their van der Waals radii.

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Chemotactic Peptide Analogs: Conformation of *N*-Formyl-L-methionyl-N^2-methyl-L-phenylalanine *tert*-Butyl Ester

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Abstract. $C_{20}H_{30}N_2O_4S$, $M_r = 394·54$, orthorhombic, $P2_12_12_1$, $a = 8·803$ (3), $b = 9·480$ (9), $c = 26·047$ (20) Å, $V = 2174$ (3) Å^3, $Z = 4$, $D_m = 1·21$ (2) (flotation in aqueous $ZnCl_2$), $D_x = 1·205$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·662$ cm^{-1}, $F(000) = 848$, $T = 253$ K, $R = 0·076$ for 1872 observations, $I \geq$

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