Crystal Structure of 1-*N*-Methyl[2,2']spiro-acenaphthene-1'-one[3,2'']spiro-cyclohexane-1''-one-4-[*p*-methylphenyl]pyrrolidine

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The title compound (C₂₈H₂₇NO₂) crystallizes in monoclinic space group *P*₂₁/*c* with a molecule in the asymmetric unit. The structure was solved by direct methods and refined by full-matrix least-squares procedures to final *R* = 0.0788 and *wR* = 0.2022 using 3083 reflections. The pyrrolidine and cyclohexane rings adopt *envelope* and *chair* conformations, respectively. The molecules are stabilized by C-H...O type intra and intermolecular interactions in addition to van der Waals forces.

(Received October 8, 2005; Accepted February 7, 2006; Published on web April 20, 2006)

Spiro-indole-pyrrolidine ring systems are frequently encountered structural motif in many pharmacologically relevant alkaloids.¹ A new class of spiro pyrrolidines has been screened for their antibacterial and antifungal activity against ten human pathogenic bacteria and four dermatophytic fungi.² Several optically active pyrrolidines have been used as intermediates in controlled synthesis.³ The resulting functionality, due to ease of substitution and modification at several positions have been utilized to synthesize compounds with varying properties. In view of these, the structure of title compound is determined to establish the conformation of the molecule (Fig. 1).

In an one spot synthesis, the '*E*' isomer of *p*-methylbenzylidene cyclohexanone was treated with one equimolar amount of acenaphthaquinone and sarcosine to obtain the title compound. The crystal and experimental details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final reliability value of 0.0788. All the non-hydrogen atoms were refined anisotropically and H atoms located from the difference Fourier were refined isotropically. The atomic coordinates and temperature factors for the non-hydrogen atoms are presented in

Fig. 1 Chemical diagram of the molecule.

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Table 2.

A ZORTEP plot of the molecule is shown in Fig. 2. The selected bond lengths, bond angles and torsion angles are listed in Table 3. The C-C and N-C bond lengths in the pyrrolidine moiety are slightly longer than the normal values. This may be

Table 1 Crystal and experimental data

CCDC No.	285851
Empirical formula	C ₂₈ H ₂₇ NO ₂
Formula weight	409.51
Crystal system	monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 18.237(9) Å <i>b</i> = 8.310(4) Å <i>c</i> = 14.563(7) Å <i>β</i> = 101.279(9)°
<i>Z</i>	4
<i>V</i>	2164.3(2) Å ³
<i>T</i>	293 K
<i>D_x</i>	1.257 Mg/m ³
<i>μ</i>	0.078 mm ⁻¹
Radiation (Mo <i>K</i> _α)	<i>λ</i> = 0.71073 Å
<i>F</i> (0 0 0)	872
<i>θ</i> range for data collection	2.28 to 27.02°
Reflections collected/unique	15914/4364
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4364/0/388
Goodness-of-fit on <i>F</i> ²	1.083
Final <i>R</i> indices [3083 refs. <i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0788, <i>wR</i> ₂ = 0.2022
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1125, <i>wR</i> ₂ = 0.2264
(Δρ) _{max}	0.304 e Å ⁻³
(Δρ) _{min}	-0.268 e Å ⁻³
Measurement	Siemens SMART CCD
Program system	SAINT
Structure determination	SHELXS97
Structure refinement	SHELXL97
Structure drawing	ZORTEP

Table 2 Atomic coordinates and temperature factors

Atom	x	y	z	U_{eq}
N1	2493(1)	-1449(3)	2138(2)	45(1)
C2	2817(1)	-618(3)	1419(2)	36(1)
C3	2365(1)	1050(3)	1263(2)	33(1)
C4	1796(1)	865(3)	1951(2)	38(1)
C5	1712(2)	-932(4)	2012(3)	48(1)
C6	2760(2)	-1633(3)	500(2)	45(1)
C7	3516(2)	-1891(3)	312(2)	41(1)
C8	3781(2)	-2659(4)	-387(3)	55(1)
C9	4554(2)	-2684(4)	-336(3)	62(1)
C10	5052(2)	-2016(4)	400(2)	54(1)
C11	4800(2)	-1236(3)	1138(2)	41(1)
C12	5235(2)	-528(4)	1942(2)	49(1)
C13	4894(2)	124(4)	2613(2)	47(1)
C14	4105(2)	156(3)	2523(2)	41(1)
C15	3668(1)	-473(3)	1743(2)	36(1)
C16	4015(1)	-1189(3)	1058(2)	36(1)
O17	2182(1)	-2218(3)	62(2)	66(1)
C18	2897(1)	2475(3)	1564(2)	38(1)
C19	3332(2)	3108(4)	854(2)	51(1)
C20	2875(2)	3291(4)	-129(2)	56(1)
C21	2452(2)	1769(4)	-438(2)	57(1)
C22	1947(2)	1324(4)	248(2)	45(1)
O23	2962(1)	3084(2)	2323(2)	49(1)
C24	1093(1)	1879(3)	1702(2)	41(1)
C25	419(2)	1313(4)	1189(3)	60(1)
C26	-197(2)	2323(5)	948(3)	68(1)
C27	-158(2)	3924(4)	1199(2)	53(1)
C28	506(2)	4467(4)	1740(3)	56(1)
C29	1118(2)	3472(4)	1979(2)	50(1)
C30	-811(2)	5043(7)	882(4)	73(1)
C31	2617(2)	-3166(4)	2215(3)	57(1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

Fig. 2 ORTEP plot of the molecule drawn at the 30% probability level.

due to the steric forces caused by the bulky substitutions at C2, C3 and C4 in pyrrolidine ring.⁴ The sum of the angles around N1 (338.5°) is in accordance with sp^3 hybridization.

The acenaphthene moiety is planar and the bond lengths are comparable to the literature values.⁵ A least-squares plane calculated through the N1, C2, C3 and C4 atoms describes the best plane of the pyrrolidine ring, wherein atom C5 deviates from the plane by 0.683(4) Å. This implies that the pyrrolidine ring adopts an *envelope* conformation. In cyclohexane, the best least-squares plane omits atoms C3 and C20, which deviate by -0.560(2) Å and 0.635(4) Å, respectively, revealing that the ring adopts a *chair* conformation. The asymmetry parameters $q_2 = 0.112(3)$, and $q_3 = 0.508(3)$, and the puckering amplitudes, $Q_T = 0.520(2)$ and $\theta = 12.4(3)^\circ$, also support the above fact.

Table 3 Selected bond distances (Å), bond angles (°) and torsion angles (°)

(i) Bond distance (Å)			
N1-C2	1.472(3)	C3-C4	1.584(3)
N1-C5	1.464(4)	C4-C5	1.507(4)
N1-C31	1.449(4)	C6-O17	1.221(4)
C2-C3	1.601(3)	C18-O23	1.202(3)
(ii) Bond angles (°)			
C2-N1-C5	106.8(2)	C5-N1-C31	115.6(3)
C2-N1-C31	116.2(2)	C7-C6-O17	126.1(3)
C2-C6-O17	124.5(2)	C19-C18-O23	120.8(3)
C3-C18-O23	121.8(2)		
(iii) Torsion angles (°)			
N1-C5-C4-C3	45.0(3)	C5-C4-C3-C2	-26.1(3)
C2-N1-C5-C4	-48.6(3)	C18-C19-C20-C21	-50.6(4)
C3-C2-N1-C5	30.9(3)	C19-C20-C21-C22	57.5(4)
C3-C18-C19-C20	44.4(4)	C20-C21-C22-C3	-59.5(4)
C4-C5-N1-C31	-179.6(3)	C21-C22-C3-C18	49.4(3)
C4-C3-C2-N1	-1.9(3)	C22-C3-C18-C19	-41.9(3)

Both the cyclohexane ring and the acenaphthene moiety are nearly orthogonal to the central pyrrolidine ring [87.4(1°) & 88.5(1°)], whereas the phenyl ring is oriented at an angle of 67.6(1°). The molecules are stabilized by the C-H...O type of intra and intermolecular interactions, which stabilize the molecules in the unit cell in addition to the van der Waals forces.

Acknowledgements

One of the authors, KP, thanks the University of Madras for providing the financial support under the 'University With Potential for Excellence' Programme.

Supplementary Material

CCDC 245940 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk.

References

1. G. Cravotta, G. B. Giovenzana, T. Pilati, M. Sisti, and G. Palmisano, *J. Org. Chem.*, **2001**, 66, 8447.
2. A. Raj, R. Raghunathan, M. R. Sridevi Kumari, and N. Raman, *Bioorg. Med. Chem.*, **2003**, 11, 407.
3. T. Suzuki, T. Nagasu, H. Kawai, K. Fujiwara, and T. Tsuji, *Tetrahedron Lett.*, **2003**, 44, 6095.
4. A. Abdul Ajees, S. Manikandan, and R. Raghunathan, *Acta Cryst.*, **2002**, E58, o802.
5. J. M. Edwards, M. Mangion, J. B. Anderson, M. Rapposch, P. Moews, and G. Hite, *Acta Cryst.*, **1980**, B36, 1241.