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Crystal Structure of 1-Hexyl-4-(4-Isothio-Cyantophenyl)Bicyclo[2,2,2] Octane

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Crystal structure of 1-hexyl-4-(4-isothiocyantophenyl)bicyclo[2,2,2] octane $C_{21}H_{29}NS$, crystallises in the triclinic space group $P\bar{1}$ with $a = 20.821(9)$Å, $b = 21.647(9)$Å, $c = 9.904(4)$Å, $\alpha = 92.53(4)°$, $\beta = 91.83(4)°$, $\gamma = 116.96°$, $V = 3968(3)$Å^3 $Z = 8$, $D_{(cal)} = 1.090$ Mg/m^3, $\mu = 0.164$ mm^{-1}, $F_{000} = 1424$, $R1 = 0.10$.

Keywords: Crystal structure; nematic

INTRODUCTION

It will be useful to undertake crystal structure studies of mesogens to understand the phase transitions and physical behaviour. 1-hexyl-4-(4-isothiocyantophenyl)bicyclo[2,2,2]octane (HICPO) compound was obtained from Aldrich Chemicals and was recrystallized in acetone. The compound exhibits nematic phase in the temperature range 50–90°C. This was confirmed by DSC studies.

EXPERIMENTAL

A crystal with approximate size $0.1 \times 0.1 \times 0.15$ mm^3 was mounted on Rigaku AFC7S diffractometer equipped with a graphite monochromated Mo$K\alpha$ X-ray source ($\lambda = 0.71069$Å). The unit cell parameters were obtained by using the method of short vectors followed by least-squares refinement of 19 reflections. All reflections could be indexed with respect to a triclinic cell. Lorentz, polarisation and empirical absorption corrections were applied. The data were reduced using teXsan [1] data reduction program. The structure was

solved by direct methods using SHELXS-97 [2]. The peak list from SHELXS-97 revealed the partial structure. Successive difference Fourier maps gave the positions of other non-hydrogen atoms. The structure was refined by full matrix least-squares using SHELXL-97 [3] with isotropic temperature factors for all non-hydrogen atoms which converged the residual to 0.21. The hydrogen atoms were generated at chemically acceptable positions and were not refined. The non-hydrogen atoms were refined anisotropically. The final cycle of full matrix least-squares refinement was done based on 5704 reflections and 834 parameters which converged to $R = 0.10$ with $I > 2\sigma(I)$. The maximum and minimum peaks on the final difference Fourier map correspond to 0.246 and -0.185 $e^{-}.Å^{-3}$ respectively.

RESULTS AND DISCUSSION

There are four molecules of HICPO in the asymmetric unit. The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table 1. Figure 1 represents the ORTEP [4] diagram of one of the molecules. Figure 2 shows packing of molecules in the unit cell down *c* axis. It can be seen that the molecules are fully extended and are parallel to the *b* axis. There is an overlap of alkyl chains along the length of the molecule. There are several intermolecular distances shorter than the van der Waal's radii. This suggests that the intermolecular interactions are mainly due to van der Waal's forces. The bond distances and bond angles compare well with those of 4-isothiocyanato phenyl 4-pentylbicyclo[2,2,2] octane-1-carboxylate (IPPOC) [5]. The melting point of the mesogen under investigation is very much less than the melting point of IPPOC which is 74.5°C. This can be surmised as due to the absence of carbonyl dipoles and a longer flexible alkyl chain. This is also suggested by the higher thermal parameters of a number of atoms which is due to positional disorder of the atoms. The phenyl rings of all the molecules are planar. The bicyclo rings of all the molecules when considered as two cyclohexane rings exhibit boat conformation as found in IPPOC. The range of the nematic phase in IPPOC and HICPO is almost same. The packing of the molecules show imbrication as expected for a nematogen.

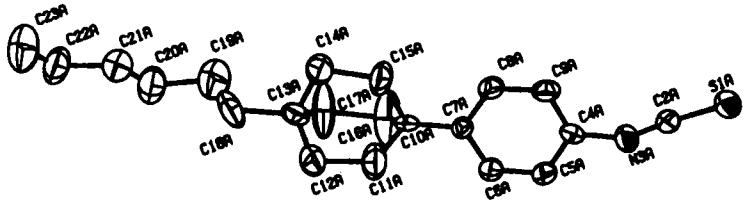

Figure 1: ORTEP of the molecule.

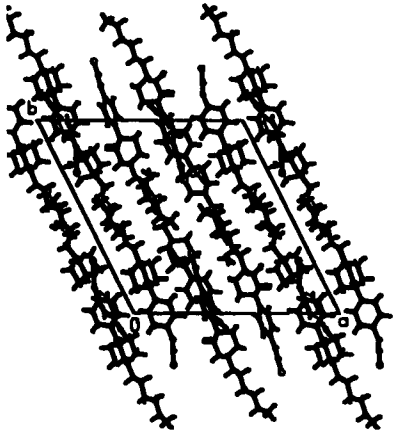

Figure 2: Packing of molecules down *c* axis.

Table 1. Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms.

Atom	x	y	z	U_{eq}
S1A	0.5771(2)	0.1000(2)	0.6082(4)	0.1990(15)
C2A	0.6050(7)	0.0434(8)	0.5883(12)	0.152(5)
N3A	0.6299(6)	0.0069(7)	0.5678(11)	0.175(4)
C4A	0.6299(11)	-0.0573(10)	0.5726(10)	0.127(4)
C5A	0.6895(9)	-0.0628(9)	0.5416(12)	0.163(4)
C6A	0.6900(8)	-0.1248(13)	0.5451(11)	0.162(4)
C7A	0.6344(10)	-0.1835(8)	0.5794(11)	0.120(3)
C8A	0.5722(9)	-0.1776(9)	0.6044(11)	0.160(4)
C9A	0.5697(9)	-0.1146(14)	0.6017(12)	0.172(5)
C10A	0.6370(5)	-0.2478(8)	0.5886(10)	0.115(3)
C11A	0.6558(15)	-0.2755(10)	0.482(2)	0.371(16)
C12A	0.666(2)	-0.3431(14)	0.491(2)	0.43(2)
C13A	0.6368(12)	-0.3777(10)	0.595(2)	0.239(10)
C14A	0.5710(9)	-0.3789(9)	0.631(3)	0.356(15)
C15A	0.5712(10)	-0.3070(10)	0.612(3)	0.355(15)
C16A	0.6841(13)	-0.2512(9)	0.693(2)	0.378(15)
C17A	0.6769(18)	-0.3288(14)	0.690(3)	0.42(2)
C18A	0.6423(13)	-0.4510(15)	0.609(3)	0.307(15)
C19A	0.633(2)	-0.476(2)	0.691(4)	0.48(4)
C20A	0.6507(18)	-0.5411(15)	0.691(4)	0.46(3)
C21A	0.6218(16)	-0.5939(15)	0.698(2)	0.302(11)
C22A	0.6328(15)	-0.6604(12)	0.706(3)	0.329(14)
C23A	0.5892(17)	-0.7177(13)	0.675(4)	0.420(19)

Table 1 continued...

Atom	x	y	z	U_{eq}
S1B	0.5734(2)	-0.3114(3)	0.0773(4)	0.2235(19)
C2B	0.5896(8)	-0.2370(10)	0.0603(15)	0.167(6)
N3B	0.6041(7)	-0.1800(9)	0.0403(16)	0.204(7)
C4B	0.6117(7)	-0.1106(10)	0.056(2)	0.149(5)
C5B	0.5914(6)	-0.0890(11)	0.1693(18)	0.148(4)
C6B	0.6000(6)	-0.0215(12)	0.1789(15)	0.144(4)
C7B	0.6304(7)	0.0251(9)	0.0865(18)	0.124(4)
C8B	0.6505(6)	0.0009(11)	-0.0312(15)	0.162(5)
C9B	0.6414(8)	-0.0679(14)	-0.0443(19)	0.181(6)
C10B	0.6384(6)	0.0976(9)	0.1019(12)	0.127(3)
C11B	0.5657(8)	0.0962(7)	0.0949(17)	0.267(8)
C12B	0.5770(10)	0.1732(10)	0.121(2)	0.310(11)
C13B	0.6485(8)	0.2235(8)	0.1352(19)	0.169(5)
C14B	0.6872(14)	0.2176(11)	0.022(2)	0.43(2)
C15B	0.6807(11)	0.1456(10)	-0.0008(19)	0.330(12)
C16B	0.6737(10)	0.1318(9)	0.229(2)	0.331(12)
C17B	0.6792(12)	0.2037(11)	0.250(2)	0.351(15)
C18B	0.6592(9)	0.2995(13)	0.1435(18)	0.260(9)
C19B	0.6378(16)	0.3238(13)	0.230(3)	0.404(19)
C20B	0.6534(13)	0.4016(13)	0.231(3)	0.336(14)
C21B	0.6206(12)	0.4293(13)	0.1785(19)	0.265(9)
C22B	0.6314(11)	0.5012(10)	0.189(2)	0.267(9)
C23B	0.5929(14)	0.5222(13)	0.107(2)	0.389(17)

Table 1 continued...

Atom	x	y	z	U_{eq}
S1C	0.9325(3)	0.2719(2)	0.1631(4)	0.237(2)
C2C	0.9009(7)	0.1957(9)	0.1677(11)	0.145(4)
N3C	0.8734(8)	0.1356(8)	0.1763(11)	0.179(5)
C4C	0.8686(12)	0.0687(10)	0.1682(11)	0.141(5)
C5C	0.9297(9)	0.0603(10)	0.1478(10)	0.154(5)
C6C	0.9218(9)	-0.0073(13)	0.1377(10)	0.142(4)
C7C	0.8609(11)	-0.0663(10)	0.1557(9)	0.126(4)
C8C	0.8010(8)	-0.0561(9)	0.1822(12)	0.173(5)
C9C	0.8068(10)	0.0100(14)	0.1836(11)	0.165(4)
C10C	0.8556(5)	-0.1368(9)	0.1415(10)	0.113(3)
C11C	0.9213(9)	-0.1366(8)	0.085(2)	0.301(10)
C12C	0.9114(11)	-0.2125(11)	0.064(2)	0.317(12)
C13C	0.8486(8)	-0.2623(8)	0.116(2)	0.172(5)
C14C	0.8440(13)	-0.2398(10)	0.250(2)	0.346(15)
C15C	0.8556(11)	-0.1638(9)	0.2720(15)	0.321(12)
C16C	0.8045(12)	-0.1791(10)	0.048(3)	0.416(18)
C17C	0.7937(11)	-0.2541(10)	0.025(2)	0.396(17)
C18C	0.8399(11)	-0.3374(13)	0.1106(19)	0.269(8)
C19C	0.8663(15)	-0.3608(13)	0.041(3)	0.45(2)
C20C	0.8445(18)	-0.446(2)	0.042(5)	0.39(2)
C21C	0.8908(17)	-0.458(2)	0.074(3)	0.339(18)
C22C	0.876(2)	-0.5370(14)	0.064(4)	0.40(2)
C23C	0.892(3)	-0.5707(15)	0.117(5)	0.53(3)

Table 1 continued...

Atom	x	y	z	U_{eq}
S1D	0.91529(18)	-0.1946(2)	-0.3671(3)	0.1851(15)
C2D	0.9055(6)	-0.1300(7)	-0.3526(11)	0.132(4)
N3D	0.8966(6)	-0.0815(7)	-0.3411(12)	0.182(5)
C4D	0.8889(7)	-0.0198(9)	-0.336(2)	0.158(6)
C5D	0.8615(7)	0.0025(11)	-0.2265(16)	0.184(6)
C6D	0.8575(6)	0.0642(9)	-0.2323(15)	0.165(4)
C7D	0.8786(5)	0.1045(7)	-0.3415(16)	0.119(3)
C8D	0.9049(5)	0.0801(9)	-0.4484(11)	0.148(4)
C9D	0.9090(6)	0.0172(9)	-0.4402(17)	0.163(5)
C10D	0.8705(6)	0.1714(7)	-0.3453(10)	0.121(3)
C11D	0.8632(13)	0.1986(10)	-0.2107(18)	0.359(13)
C12D	0.8597(17)	0.2686(14)	-0.227(3)	0.383(19)
C13D	0.8514(9)	0.2855(10)	-0.357(3)	0.209(8)
C14D	0.9285(12)	0.3001(8)	-0.398(2)	0.322(11)
C15D	0.9355(8)	0.2312(9)	-0.3916(18)	0.272(8)
C16D	0.8075(9)	0.1621(8)	-0.423(2)	0.352(13)
C17D	0.8021(14)	0.2298(14)	-0.426(3)	0.44(2)
C18D	0.8379(10)	0.3466(12)	-0.359(2)	0.256(8)
C19D	0.8750(11)	0.4000(13)	-0.409(3)	0.352(15)
C20D	0.8544(10)	0.4635(12)	-0.404(3)	0.300(10)
C21D	0.8920(15)	0.5206(15)	-0.440(3)	0.42(2)
C22D	0.877(2)	0.580(2)	-0.438(5)	0.44(2)
C23D	0.865(2)	0.6098(18)	-0.467(5)	0.40(2)

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