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## Dynamic Conformational Behaviour of an Eleven-Membered Ring in the Solid State. X-ray Studies of Cycloundecylmethyl 1-Naphthylcarbamate at 120 and 293 K

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### Abstract

The crystal structure of cycloundecylmethyl 1-naphthylcarbamate is ordered at 120 K and the eleven-membered ring exhibits the [12323] conformation of cycloundecane with C—C(*sp*<sup>3</sup>)—C angles enlarged beyond tetrahedral, 112.1–118.4 (3)°. The crystal structure is disordered at 293 K in the region occupied by the eleven-membered ring and molecular-mechanics calculations establish that the major component of the conformational mixture has the [335] cycloundecane conformation. X-ray studies at 293 K before and after cooling a crystal to 120 K for *ca* 120 h confirmed that the order–disorder transformation is reversible. The [12323] ⇌ [335] conformational interconversion has been detected previously for cycloundecane in solution. C<sub>23</sub>H<sub>31</sub>NO<sub>2</sub>, *M<sub>r</sub>* = 353.54, monoclinic, *P*2<sub>1</sub>/*c*, *Z* = 4, λ(Cu *Kα*) = 1.5418 Å, *F*(000) = 768. At 293 K, *a* = 8.789 (3), *b* = 26.393 (4), *c* = 9.237 (2) Å, β = 107.33 (2)°, *V* = 2045 (1) Å<sup>3</sup>, *D<sub>x</sub>* = 1.15 Mg m<sup>-3</sup>, μ = 0.57 mm<sup>-1</sup>, *R* = 0.079 for 2288 independent reflections with *I* > 2.5σ(*I*); *a* = 8.792 (2), *b* = 26.394 (3), *c* = 9.239 (1) Å, β = 107.35 (2)°, *V* = 2046 (1) Å<sup>3</sup>, *R* = 0.073 for 2185 reflections with *I* > 2.5σ(*I*). At 120 K, *a* = 8.568 (3), *b* = 26.227 (5), *c* = 9.183 (2) Å, β = 107.91 (2)°, *V* = 1964 (1) Å<sup>3</sup>, *D<sub>x</sub>* = 1.20 Mg m<sup>-3</sup>, μ = 0.59 mm<sup>-1</sup>, *R* = 0.049 for 3055 independent reflections with *I* > 2.5σ(*I*).

### Introduction

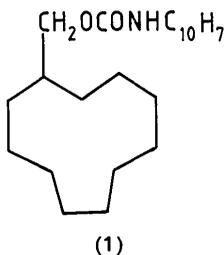
Equilibria involving conformational interconversions of organic molecules in liquids have been extensively

studied (Eliel, Allinger, Angyal & Morrison, 1965; Riddell, 1980; Berg & Sandström, 1986, 1987) but few analogous transformations in solids have been recognized, though a variety of other processes involving atomic and molecular displacements in crystals are known (Gavezzotti & Simonetta, 1987; Bernstein, 1987). A dynamic equilibrium between two or more conformers in a single crystal will result in a disordered crystal structure and the population of various conformers at the disordered site will vary with temperature in accord with the Boltzmann distribution. X-ray structural analyses at several temperatures have characterized chair ⇌ boat interconversion of six-membered rings in some derivatives of bicyclo[3.3.1]nonan-9-one (G. A. Sim, unpublished results) and axial ⇌ equatorial interchange at the N atoms in 1,3,5-tribenzyl-1,3,5-triazacyclohexane (Sim, 1987). Cycloundecane undergoes facile conformational exchange in solution at low temperatures (Anet, Cheng & Wagner, 1972) and this prompted us to investigate compounds incorporating eleven-membered rings.

Force-field calculations for cycloundecane have identified six conformations within an energy span of 11 kJ mol<sup>-1</sup>, with the two lowest-energy conformations, [335] and [12323], being nearly identical in strain energy (Anet & Rawdah, 1978). The NMR spectra of cycloundecane demonstrate conformational exchange in solution down to *ca* 120 K and this has been interpreted in terms of interconversion of the [335] and [12323] forms and pseudorotation of the former (Anet & Rawdah, 1978). Conformational data for simple derivatives of cycloundecane in the solid state are sparse; X-ray results for cycloundeca-

none (Groth, 1974) and its oxime (Groth, 1979) at *ca* 110 K establish that the former adopts the [335] conformation and the latter the [12323] conformation. Caprinolactam hemihydrochloride (Winkler & Dunitz, 1975) can also be compared with these compounds and the conformation in the crystal is of the [335] type.

An X-ray crystallographic investigation of cycloundecylmethyl 1-naphthylcarbamate (1) at 120 and 293 K was undertaken to obtain conformational information about a cycloundecane with a single substituent.



### Experimental

Compound (1) was prepared from cycloundecylmethanol by reaction with 1-naphthyl isocyanate (Vogel, 1978).

Colourless crystals, dimensions  $0.15 \times 0.30 \times 0.40$  mm. Enraf-Nonius diffractometer,  $\text{Cu K}\alpha$  radiation, generator settings 43 kV, 26 mA. Cell dimensions from setting angles of 25 independent reflections with  $\theta$   $15\text{--}24^\circ$  (293 K, initial analysis),  $19\text{--}31^\circ$  (120 and 293 K, final analysis). Initially, at 293 K, 4013 reflections surveyed in range  $2\text{--}72^\circ$ ,  $h$   $0 \rightarrow 10$ ,  $k$   $0 \rightarrow 32$ ,  $l$   $-11 \rightarrow 11$ ; scan width  $(0.76 + 0.14 \tan \theta)^\circ$ ; maximum counting time 120 s; 2288 independent reflections with  $I > 2.50\sigma(I)$ . At 120 K, with a different crystal, 3681 reflections surveyed in range  $1.5\text{--}65^\circ$ ; scan width  $(1.0 + 0.3 \tan \theta)^\circ$ ; maximum counting time 120 s; 3325 independent reflections, 3055 with  $I > 2.5\sigma(I)$ ,  $R_{\text{int}} = 0.044$ . At 293 K, with the crystal used for data collection at 120 K, 3823 reflections surveyed in range  $1.5\text{--}65^\circ$ ; scan width  $(1.0 + 0.3 \tan \theta)^\circ$ ; maximum counting time 120 s; 3480 independent reflections, 2185 with  $I > 2.5\sigma(I)$ ,  $R_{\text{int}} = 0.045$ . Two reference reflections monitored periodically showed no significant variation in intensity. No absorption or extinction correction.

In the initial analysis at 293 K, the atoms of the 1-naphthylcarbamate moiety and atoms C(1), C(2), C(11) of the cycloundecane ring were located by direct phasing using *MULTAN* (Germain, Main & Woolfson, 1971). A weighted Fourier synthesis based on these atoms led to the identification of C(3), C(8), C(9), C(10). Sites for the atoms C(4), C(5), C(6), C(7) of the remaining section of the eleven-membered ring

were obtained from subsequent difference Fourier syntheses but there were always additional small peaks in this region, suggesting disorder. Some of the H atoms were identified in the difference maps. In the least-squares refinement the C, N and O atoms were assigned anisotropic thermal parameters and the H atoms were placed in ideal positions with isotropic thermal parameters; no attempt was made to include additional atoms in the disordered region or to adjust occupation parameters. Refinement of this model converged to  $R = 0.079$ ,  $wR = 0.097$ , with  $w = 1/\sigma^2(|F_o|)$ ,  $\Delta/\sigma < 0.5$ , final  $\Delta\rho$  maximum  $0.29$ , minimum  $-0.24 \text{ e } \text{\AA}^{-3}$ , largest residual electron density in the C(3)···C(8) region. Fourier, least-squares and geometry calculations were performed with *SHELX* (Sheldrick, 1976). The residual electron density, the large thermal ellipsoids and the anomalous bond lengths and angles in the C(3)···C(8) segment of the eleven-membered ring are indicative of disorder involving the presence of more than one conformation in the crystal (Dunitz & Eser, 1967; Dunitz, Eser, Bixon & Lifson, 1967).

The 120 K crystal structure was elucidated by direct phasing with *MITHRIL* (Gilmore, 1984) which showed only 11 peaks in the cycloundecane region. After preliminary least-squares adjustment of the C, N and O atoms ( $R = 0.11$ ) all 31 H atoms were located in a difference electron-density map, with peak heights of  $0.82\text{--}0.44 \text{ e } \text{\AA}^{-3}$ . Full-matrix least-squares calculations on  $F$  with anisotropic thermal parameters for the C, N and O atoms and isotropic for the H atoms converged at  $R = 0.049$ ,  $wR = 0.054$ , with  $\Delta/\sigma < 0.2$ ,  $w = 1$ , final  $\Delta\rho$  maximum  $0.16$ , minimum  $-0.20 \text{ e } \text{\AA}^{-3}$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Calculations performed with the *GX* system of programs (Mallinson & Muir, 1985).

To investigate the reversibility of the transformation between disordered and ordered conformational states, the crystal used for data collection at 120 K was warmed to room temperature, 293 K, X-ray intensity data recollected and the crystal structure redetermined. The 1-naphthylcarbamate group was used as the starting point in the calculations and the remaining C atoms located in difference maps. As in the initial 293 K analysis, additional small peaks in the C(3)···C(8) ring segment were ignored. Some of the H atoms were located in difference electron-density maps and the remainder placed by geometrical considerations. Full-matrix least-squares adjustment of the coordinates and anisotropic thermal parameters for the C, N and O atoms and isotropic thermal parameters for the H atoms converged at  $R = 0.073$ ,  $wR = 0.097$ , with  $\Delta/\sigma < 0.5$ ,  $w = 1/\sigma^2(|F_o|)$ , final  $\Delta\rho$  maximum  $0.25$ , minimum  $-0.26 \text{ e } \text{\AA}^{-3}$ . Calculations performed as in the 120 K analysis. The final molecular structure derived

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for compound (1) at 120 K

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$$

	x	y	z	$U_{\text{eq}}$
C(1)	0.3747 (3)	0.1460 (1)	0.9323 (3)	0.026
C(2)	0.5260 (3)	0.1819 (1)	0.9809 (3)	0.031
C(3)	0.5462 (3)	0.2174 (1)	1.1187 (3)	0.035
C(4)	0.6121 (3)	0.1920 (1)	1.2761 (3)	0.035
C(5)	0.4791 (3)	0.1675 (1)	1.3337 (3)	0.032
C(6)	0.5432 (4)	0.1299 (1)	1.4667 (3)	0.041
C(7)	0.6260 (4)	0.0813 (1)	1.4339 (3)	0.042
C(8)	0.5109 (4)	0.0397 (1)	1.3410 (3)	0.041
C(9)	0.4132 (3)	0.0517 (1)	1.1746 (3)	0.030
C(10)	0.5196 (3)	0.0669 (1)	1.0744 (3)	0.029
C(11)	0.4235 (3)	0.0900 (1)	0.9206 (3)	0.030
C(12)	0.2589 (3)	0.1622 (1)	0.7793 (3)	0.030
C(13)	0.1193 (3)	0.2386 (1)	0.6733 (3)	0.024
C(14)	0.0033 (3)	0.3255 (1)	0.6183 (3)	0.024
C(15)	0.0114 (3)	0.3745 (1)	0.6883 (3)	0.025
C(16)	0.0806 (3)	0.3832 (1)	0.8477 (3)	0.030
C(17)	0.0879 (3)	0.4310 (1)	0.9085 (3)	0.036
C(18)	0.0243 (3)	0.4735 (1)	0.8135 (3)	0.038
C(19)	-0.0435 (3)	0.4666 (1)	0.6604 (3)	0.035
C(20)	-0.0521 (3)	0.4174 (1)	0.5915 (3)	0.028
C(21)	-0.1159 (3)	0.4108 (1)	0.4322 (3)	0.033
C(22)	-0.1198 (3)	0.3636 (1)	0.3699 (3)	0.031
C(23)	-0.0619 (3)	0.3204 (1)	0.4624 (3)	0.027
N(1)	0.0659 (2)	0.2833 (1)	0.7146 (2)	0.024
O(1)	0.2030 (2)	0.2131 (1)	0.8000 (2)	0.028
O(2)	0.0990 (2)	0.2228 (1)	0.5446 (2)	0.035

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for compound (1) at 120 K

C(1)—C(2)	1.552 (4)	C(1)—C(11)	1.541 (4)
C(1)—C(12)	1.510 (4)	C(2)—C(3)	1.537 (4)
C(3)—C(4)	1.533 (4)	C(4)—C(5)	1.538 (4)
C(5)—C(6)	1.533 (4)	C(6)—C(7)	1.533 (5)
C(7)—C(8)	1.540 (5)	C(8)—C(9)	1.533 (4)
C(9)—C(10)	1.533 (4)	C(10)—C(11)	1.525 (4)
C(12)—O(1)	1.452 (3)	C(13)—N(1)	1.355 (3)
C(13)—O(1)	1.342 (3)	C(13)—O(2)	1.213 (3)
C(14)—C(15)	1.431 (4)	C(14)—C(23)	1.374 (4)
C(14)—N(1)	1.415 (3)	C(15)—C(16)	1.418 (4)
C(15)—C(20)	1.433 (4)	C(16)—C(17)	1.367 (4)
C(17)—C(18)	1.415 (4)	C(18)—C(19)	1.358 (5)
C(19)—C(20)	1.429 (4)	C(20)—C(21)	1.406 (4)
C(21)—C(22)	1.361 (4)	C(22)—C(23)	1.410 (4)
C(2)—C(1)—C(11)	112.1 (2)	C(2)—C(1)—C(12)	110.4 (2)
C(11)—C(1)—C(12)	108.5 (2)	C(1)—C(2)—C(3)	118.4 (3)
C(2)—C(3)—C(4)	115.4 (3)	C(3)—C(4)—C(5)	114.2 (3)
C(4)—C(5)—C(6)	114.9 (3)	C(5)—C(6)—C(7)	116.9 (3)
C(6)—C(7)—C(8)	116.2 (3)	C(7)—C(8)—C(9)	117.9 (3)
C(8)—C(9)—C(10)	114.1 (3)	C(9)—C(10)—C(11)	114.0 (3)
C(1)—C(11)—C(10)	113.3 (3)	C(1)—C(12)—O(1)	106.5 (2)
N(1)—C(13)—O(1)	108.9 (2)	N(1)—C(13)—O(2)	127.5 (3)
O(1)—C(13)—O(2)	123.6 (3)	C(15)—C(14)—C(23)	120.2 (3)
C(15)—C(14)—N(1)	117.8 (2)	C(23)—C(14)—N(1)	122.0 (3)
C(14)—C(15)—C(16)	123.7 (3)	C(14)—C(15)—C(20)	118.1 (3)
C(16)—C(15)—C(20)	118.3 (3)	C(15)—C(16)—C(17)	121.3 (3)
C(16)—C(17)—C(18)	120.6 (3)	C(17)—C(18)—C(19)	119.7 (3)
C(18)—C(19)—C(20)	121.7 (3)	C(15)—C(20)—C(19)	118.4 (3)
C(15)—C(20)—C(21)	120.0 (3)	C(19)—C(20)—C(21)	121.5 (3)
C(20)—C(21)—C(22)	120.1 (3)	C(21)—C(22)—C(23)	121.2 (3)
C(14)—C(23)—C(22)	120.4 (3)	C(13)—N(1)—C(14)	126.7 (2)
C(12)—O(1)—C(13)	117.0 (2)		

in this way was virtually identical to that obtained in the initial 293 K analysis, with the same evidence for conformational disorder.

## Discussion

Tables 1 and 2 list the atomic coordinates and molecular dimensions from the 120 K X-ray analysis.\* Figs. 1 and 2, drawn with ORTEP (Johnson, 1965), illustrate the molecular structures at 120 and 293 K.

The X-ray analyses establish that the cycloundecane derivative (1) adopts a single ordered conformation in the crystal at 120 K but is conformationally disordered at 293 K; moreover, the final analysis at 293 K with the crystal that had been used for the 120 K analysis produced cell dimensions and atomic coordinates extremely close to those from the initial 293 K analysis with a crystal that had not experienced a low temperature, demonstrating that the conformational transformation between 293 and

\* Lists of structure factors, anisotropic thermal parameters, torsion angles, bond lengths and angles, and atomic coordinates for the 120 and 293 K measurements have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53277 (69 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

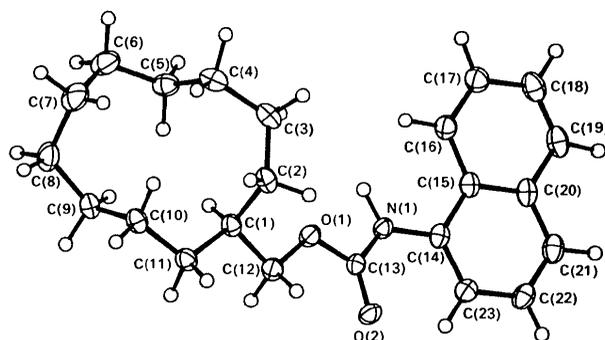


Fig. 1. Molecular structure and atomic numbering at 120 K. The thermal ellipsoids of the C, N and O atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1  $\text{\AA}$ .

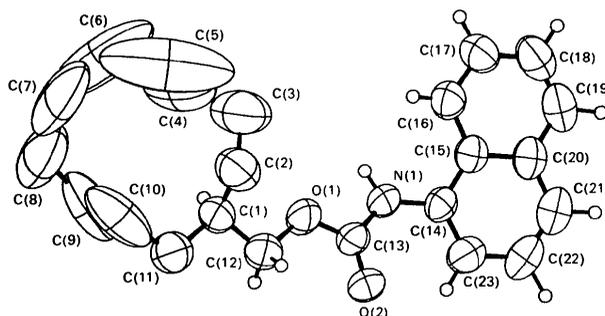


Fig. 2. Molecular structure and atomic numbering at 293 K. The thermal ellipsoids of the C, N and O atoms are drawn at the 50% probability level. The H atoms located experimentally are represented by spheres of radius 0.1  $\text{\AA}$ .

Table 3. Comparison of the torsion angles ( $^{\circ}$ ) in the eleven-membered ring of compound (1) at 120 and 293 K with force-field results for cycloundecane

	120 K	293 K		[12323]	[335] <sub>A</sub>	[335] <sub>B</sub>	[335] <sub>3A,B</sub>
11-1-2-3	-127.1 (3)	-132.2 (6),	-128.5 (7)	-128	-138	-138	-138
1-2-3-4	78.1 (3)	65.2 (9),	66.5 (8)	80	62	66	63
2-3-4-5	-86.3 (3)	85.9 (11),	88.0 (14)	-91	60	61	60
3-4-5-6	164.0 (4)	-171.1 (9),	-166.0 (12)	164	-159	-172	-162
4-5-6-7	-64.6 (3)	109.4 (14),	106.2 (19)	-65	126	66	111
5-6-7-8	-75.8 (3)	-68.3 (25),	-70.7 (25)	-75	-97	55	-59
6-7-8-9	65.9 (3)	3.8 (26),	7.2 (21)	67	55	-97	17
7-8-9-10	56.9 (3)	89.7 (11),	85.7 (12)	58	66	126	81
8-9-10-11	-167.1 (4)	-168.2 (6),	-166.4 (7)	-165	-172	-159	-169
9-10-11-1	77.6 (3)	77.0 (7),	80.7 (7)	75	61	60	61
10-11-1-2	66.5 (3)	54.9 (6),	53.3 (5)	68	66	62	65

120 K is reversible. The differences between corresponding torsional angles in the eleven-membered ring derived from the two 293 K analyses are 1.3–5.1 $^{\circ}$ , mean 2.9 $^{\circ}$ . The thermal ellipsoids in Fig. 2 show that the 1-naphthylcarbamate substituent at C(1), and atoms C(11), C(1), C(2) and C(3) of the eleven-membered ring, retain their positions during the conformational change between 120 and 293 K.

The torsional angles for the eleven-membered ring were compared with the force-field angles calculated for the six low-energy conformations of cycloundecane (Anet & Rawdah, 1978) and this established that the 120 K conformation of compound (1) is essentially identical with the Anet & Rawdah [12323] conformation (Table 3), the differences between corresponding X-ray and force-field torsional angles ranging from 0 to 5 $^{\circ}$  with a mean difference of only 2 $^{\circ}$ . In the case of the 293 K X-ray results the comparison with the force-field results proved far less satisfactory; only the Anet & Rawdah [335] conformation approximates to the X-ray results and even here the differences between corresponding X-ray and force-field torsional angles range up to 51 $^{\circ}$ , with a mean difference of 18 $^{\circ}$ , the major discrepancies being in the region of the ring where there are large apparent thermal ellipsoids (Fig. 2). These results confirm that we are dealing with a conformational mixture, rather than a single conformation, and suggest that the [335] conformation is a major constituent of the disordered mixture. Indeed, when the 293 K coordinates for the eleven-membered ring were used as the starting point for molecular-mechanics calculations for cycloundecane, using the White & Bovill (1977) force field, the calculations converged to the [335] conformation, consistent with this being an important component of the conformational mixture in the crystal of compound (1) (*cf.* Dunitz, Eser, Bixon & Lifson, 1967).

The conversion of conformation [12323] to [335], keeping atoms C(11), C(1), C(2), C(3) fixed (see Fig. 2), can take place by going anticlockwise or clockwise around the Anet & Rawdah [335] ring (see Table 3). Conformations [335]<sub>A</sub> and [335]<sub>B</sub> overlap well in the ring segment carrying the 1-

naphthylcarbamate group and differ appreciably in the ring segment remote from the substituent, where the atoms are poorly defined in the 293 K X-ray analysis. The X-ray torsional angles are closer to those of orientation [335]<sub>A</sub> than [335]<sub>B</sub> and if it is assumed that orientations *A* and *B* are present in the ratio of 2:1 or 3:1 the torsional angles appropriate to the conformational mixture differ from the X-ray results by a maximum of 26 $^{\circ}$  (28 $^{\circ}$ ) and a mean of 9 $^{\circ}$  (10 $^{\circ}$ ), where the first value of each pair refers to the initial 293 K analysis and the second value to the final 293 K analysis. The presence of two orientations of conformation [335] is equivalent to the 1-naphthylcarbamate group being located at either C(1) or C(11) of an isolated [335]<sub>A</sub> ring numbered as in Table 3. Molecular-mechanics calculations for the two analogous methylcycloundecanes with the White & Bovill force field gave steric energies that differed by no more than 0.06 kJ mol<sup>-1</sup> and this suggests that environmental factors in the crystal, rather than intramolecular steric effects, favour orientation [335]<sub>A</sub> over [335]<sub>B</sub> for compound (1).

The [12323]  $\rightleftharpoons$  [335] conformational interconversion of an eleven-membered ring is also found in crystals of cycloundecanone phenylsemicarbazone, though there the ordered low-temperature conformation is the [335] form (G. A. Sim, unpublished results). The [12323]  $\rightleftharpoons$  [335] interconversion was first noted for cycloundecane in solution, where the [335] form predominates at low temperature (Anet & Rawdah, 1978).

Most crystal structures contain a single preferred conformation but examples are known both of ordered and disordered arrangements of two or more conformers; crystals of *cyclo*-(hexaglycyl-), for example, have four distinct conformers in an ordered arrangement (Karle & Karle, 1963) whereas crystals of 1,1,5,5-tetramethylcyclodecane-8-carboxylic acid contain a disordered mixture of two conformers and the resultant approximate superposition of molecules in the averaged unit cell gives rise to anomalous features in the apparent molecular structure (Dunitz, Eser, Bixon & Lifson, 1967) similar to those observed for compound (1) at room temperature.

The observation of the [335] conformation in some and the [12323] conformation in other crystal structures of derivatives of cycloundecane at low temperatures is consistent with there being only a small difference in strain energy between these conformations. For comparison, the two lowest-energy conformations of cycloundeca-1,5-diene differ by only  $3.1 \text{ kJ mol}^{-1}$  and both conformations have been found in crystal structures of compounds with this ring system; the analogous energy difference for cycloundeca-1,6-diene is  $5.6 \text{ kJ mol}^{-1}$  and only the lowest-energy conformation of this ring system has been observed in crystal structures (Russell, Sim & Haufe, 1989). When van der Waals interactions predominate, the differences in lattice energy among polymorphic crystal forms of an organic compound range up to *ca*  $8 \text{ kJ mol}^{-1}$  (Bernstein, 1987) and molecular conformations that differ from the most stable forms by more than this amount are very unlikely to be found in the solid state. Only the [335] and [12323] conformations have been found in ordered crystal structures of derivatives of cycloundecane. In the case of a crystal structure that is conformationally disordered, the entropy component of the free energy is clearly paramount. The entropy contribution obtained when other conformers are introduced at random into the lattice appropriate to the most stable conformer is, of course, opposed by unfavourable lattice energy terms in addition to the differences in conformational energy, and conformational mixtures are expected to be met less frequently in solids than in liquids. A dynamic conformational change in a solid, moreover, requires a low barrier to the conformational interconversion and this requirement may be difficult to satisfy since only a few examples of conformational equilibria in single crystals are yet known. For the 293 K crystal structure of compound (1) we conclude that two orientations of the [335] conformation contribute appreciably to the disordered conformational mixture, that there is a residue of the [12323] conformation, and that higher-energy conformations, if present, are populated to only a small extent.

The torsional angles calculated for the [12323] and [335] conformations of cycloundecane with the White & Bovill force field are in excellent agreement with the angles calculated by Anet & Rawdah (1978), the maximum difference between corresponding angles being  $3^\circ$  and the mean difference  $1^\circ$ . We calculated a difference in strain energies between these conformations of  $2.1 \text{ kJ mol}^{-1}$ , whereas Anet & Rawdah calculated a difference of *ca*  $0.0 \text{ kJ mol}^{-1}$ . Either

result is compatible with the observation of both conformations in crystal structures of derivatives of cycloundecane. The C—C—C angles in the eleven-membered ring are larger than tetrahedral,  $112.1\text{--}118.4 (3)^\circ$ , mean  $115.2^\circ$  (X-ray, 120 K), and  $113.4\text{--}117.3^\circ$ , mean  $115.0^\circ$  (White & Bovill force field, [12323] conformation); the differences between corresponding X-ray and force-field bond angles are  $0.1\text{--}3.0^\circ$ , mean  $0.9^\circ$ .

The bond lengths in the naphthalene system of compound (1),  $1.358\text{--}1.433 (4) \text{ \AA}$ , show the variations seen in naphthalene (Cruickshank, 1957).

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