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4-*tert*-Butyl-1-aza-2-cyclohexanone

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Abstract. $C_9H_{17}NO$, monoclinic, $P2_1/c$, $a = 14\cdot674$ (4), $b = 6\cdot158$ (1), $c = 10\cdot363$ (2) Å, $\beta = 105\cdot62$ (2)° (all at 138 K), $Z = 4$, $M_r = 155\cdot24$, D_x (room temperature) $= 1\cdot101$, $D_m = 1\cdot097$ Mg m^{-3}. The final R value is $0\cdot048$ for all 1752 data. The molecule is observed in a half-chair conformation and contains a *cis*-amide bond which exhibits significant non-planar character [$\chi_N = 8\cdot5$ (15)°].

Introduction. 4-*tert*-Butyl-1-aza-2-cyclohexanone was prepared by Tichý, Malŏn, Frič & Bláha (1977) as part of a general investigation of the conformation of six-membered lactams in which the conformation was stabilized by the introduction of a *tert*-butyl group. In addition, they were able to synthesize the optically active (4*S*) isomer. The present communication deals, however, with the structure determination of the racemic mixture.

The title compound was recrystallized from diethyl ether. A cubic crystal with dimensions of 0·5 mm was selected for data collection and unit-cell determination at 138 ± 2 K using a Nonius CAD-4 automatic diffractometer. The unit-cell dimensions were determined from 42 reflections distributed throughout all octants of reciprocal space using Cu $K\alpha_1$ ($\lambda = 1\cdot5405$ Å) radiation. The intensities of 1752 reflections [1660 with $I > 2\sigma(I)$] with $2\theta \leq 150°$ were measured using θ–2θ scans and Cu $K\bar{\alpha}$ radiation. The scan angle and aperture width were $(1\cdot5 + 0\cdot15 \tan\theta)°$ and $(4\cdot0 + 0\cdot86 \tan\theta)$ mm respectively. The maximum scan time per reflection was 60 s. Crystal orientation was checked every 100 reflections and an intensity monitor was measured every 20 reflections. The intensity of the monitor reflection decreased by 4% during data collection. Lorentz and polarization factors were applied but no absorption correction was made.

The structure was solved by direct methods (Karle & Karle, 1966) using the *MULTAN* program (Germain, Main & Woolfson, 1971). The H positions were located from a difference Fourier map based on the partially refined positions of the O, N and C atoms. The structure was refined with block-diagonal least-squares techniques (Ahmed, 1966) with anisotropic thermal parameters for O, N and C atoms and isotropic thermal parameters for H atoms. Refinement was discontinued when all parameter shifts were less than one-half of the corresponding standard deviation. A final R value ($R = \sum \|kF_o| - |F_c\|/\sum |kF_o|$) of 0·048 was obtained for all data using the final parameters (Tables 1 and 2).* Scattering factors for C, N and O atoms were taken

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* Lists of structure factors, anisotropic thermal parameters and bond distances involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34599 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^5$) *for* C, N *and* O *atoms*

Standard deviations for last digit are in parentheses.

	x	y	z
N(1)	43577 (7)	109572 (18)	33948 (12)
C(2)	38299 (8)	91817 (20)	30373 (13)
O(2)	40337 (7)	77588 (16)	23114 (11)
C(3)	29621 (9)	89292 (19)	35469 (14)
C(4)	25719 (9)	110936 (18)	39025 (12)
C(5)	34014 (10)	122133 (20)	48951 (14)
C(6)	41643 (9)	127574 (21)	42026 (14)
C(7)	16541 (9)	108761 (19)	43578 (12)
C(8)	8768 (9)	98419 (25)	32281 (15)
C(9)	13064 (11)	131495 (23)	46231 (15)
C(10)	18050 (11)	95081 (22)	56253 (14)

from *International Tables for X-ray Crystallography* (1962) and those for H atoms from Stewart, Davidson & Simpson (1965). The weights of F in the least-squares calculations were determined from $\sigma(I)$, which were in turn based on counting statistics (van der Helm & Poling, 1976). In the structure factor analysis, the value of $\overline{W\Delta F^2}$ did not vary significantly with either $|F_o|$ or $\sin^2\theta$.

Discussion. A stereoview of a single molecule is shown in Fig. 1. The molecule is a six-membered lactam with a *cis*-amide group and is substituted at the 4-position by a *tert*-butyl group. Bond distances and atom numbering are shown in Fig. 2; bond angles and endocyclic torsion angles are given in Fig. 3.

The molecule is observed in a half-chair conformation (Fig. 3) with the *tert*-butyl substituent in the equatorial position. The temperature-dependent CD spectra of the compound, in various solvents, led to the same conclusion for the conformation of the molecule (Tichý *et al.*, 1977). The torsion angles for the amide group are: C(6)—N(1)—C(2)—C(3), ω_1, $-2\cdot4\ (2)°$; H(1)—N(1)—C(2)—O(2), ω_2, $6\cdot2\ (14)°$; C(6)—N(1)—C(2)—O(2), ω_3, $177\cdot7\ (1)°$; and H(1)—N(1)—C(2)—

Table 2. *Positional parameters* $(\times 10^3)$ *for* H *atoms and thermal parameters*

	x	y	z	$B\ (\text{Å}^2)$
H(1)	482 (2)	1115 (3)	304 (2)	3·9 (4)
H(31)	316 (1)	808 (3)	435 (2)	3·5 (4)
H(32)	249 (1)	805 (3)	291 (2)	3·2 (4)
H(41)	238 (1)	1211 (2)	302 (2)	1·6 (3)
H(51)	367 (1)	1124 (3)	571 (2)	2·7 (3)
H(52)	322 (1)	1364 (3)	523 (2)	2·5 (3)
H(61)	477 (1)	1319 (3)	491 (2)	3·8 (4)
H(62)	398 (1)	1405 (2)	363 (2)	2·0 (3)
H(81)	102 (1)	823 (3)	306 (2)	3·3 (4)
H(82)	25 (2)	985 (3)	343 (2)	4·2 (4)
H(83)	76 (1)	1070 (3)	241 (2)	3·2 (4)
H(91)	65 (2)	1306 (3)	481 (2)	4·1 (4)
H(92)	123 (2)	1410 (3)	382 (2)	3·9 (4)
H(93)	172 (1)	1383 (3)	545 (2)	3·3 (4)
H(101)	123 (2)	934 (4)	594 (2)	5·0 (5)
H(102)	234 (1)	1013 (3)	639 (2)	3·5 (4)
H(103)	197 (1)	789 (3)	549 (2)	3·3 (4)

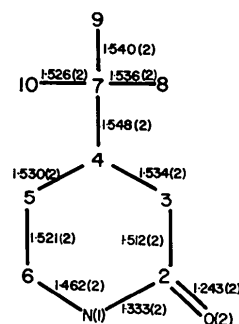Fig. 1. A stereoview of a single molecule (Johnson, 1965).

Fig. 2. Atom numbering and bond distances (Å). The N(1)—H(1) bond distance is 0·86 (2) Å. The C—H distances vary between 0·96 and 1·08 Å, and have been deposited.
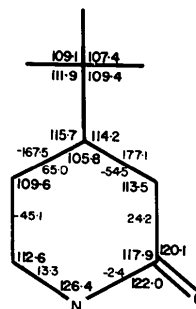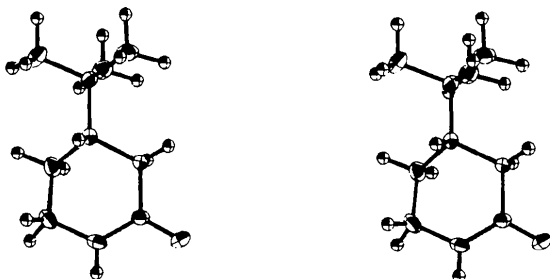
Fig. 3. Bond angles (°) (standard deviations between 0·1 and 0·2°) and torsion angles (°) (standard deviations between 0·1 and 0·2°). Additional bond angles are C(4)—C(7)—C(9) 109·5 (1), C(8)—C(7)—C(10) 109·5 (1), C(2)—N(1)—H(1) 117 (1) and C(6)—N(1)—H(1) 116 (1)°.

C(3), ω_4, $-173\cdot9\ (14)°$, using the nomenclature of Winkler & Dunitz (1971). These torsion angles yield the following values for the three independent parameters: χ_C [$= \omega_1 - \omega_3 + \pi$ (mod 2π)] $-0\cdot1\ (2)°$; χ_N [$= \omega_2 - \omega_3 + \pi$ (mod 2π)] $8\cdot5\ (15)°$; and τ [$= \frac{1}{2}(\omega_1 + \omega_2)$] $1\cdot9\ (8)°$, where the standard deviation for the last digit is given in parentheses. These results are similar to those observed for the *cis*-amide linkage in the seven-membered lactam, caprolactam (Winkler & Dunitz, 1975), which are χ_C $-0\cdot8\ (4)°$, χ_N $6\cdot5\ (30)°$ and τ $-0\cdot6\ (15)°$. The results for the present compound are somewhat more accurate and allow the conclusion that the amide bond is non-planar. This non-planarity is due only to χ_N which is 7–8 σ's different from 0°, and not to χ_C and τ. This means that the non-planarity of the amide group is caused only by the pyramidal nature of the three bonds attached to the N atom. The non-planarity of the amide group is, however, not reflected in either a shortening of the C'—O bond or a lengthening of the N—C' bond. The C(2)—O(2) bond [1·243 (2) Å], instead, is slightly longer rather than shorter when compared to those observed in planar groups: 1·23–1·24 Å (Ramachandran, Kolaskar, Ramakrishnan & Sasisekharan, 1974; Marsh & Donohue, 1967). The N(1)—C(2) bond length [1·333 (2) Å]

is nearly the same as those values predicted for planar *cis*-amide bonds: $1 \cdot 32 - 1 \cdot 34$ Å (Ramachandran & Sasisekharan, 1968; Winkler & Dunitz, 1975). If one compares the present results with a previous study on spirodilactams (Ealick & van der Helm, 1975, 1977; Ealick, Washecheck & van der Helm, 1976), it appears that the influence on the $N-C'$ and $C'-O$ distances becomes significant only when the non-planarity of the amide group is rather large, that is when $\chi_N \simeq 2\tau \geq 10-15°$.

The packing of the molecules is by H-bonding around the twofold screw axis $[N(1) \cdots O(2)(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ $2 \cdot 875$ Å; $H(1) \cdots O(2)$ $2 \cdot 071$ Å and $N(1)-H(1) \cdots O(2)$ $155°]$, and by van der Waals forces in the a and c directions.

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2,5-Distyrylpyrazine (DSP)—1,4-Bis[2-(2-pyridyl)vinyl]benzene (P2VB) (4:6); a Photopolymerizable Mixed Crystal

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Abstract. $C_{20}H_{16}N_2$ (for each compound), $M_r = 284 \cdot 4$, orthorhombic, *Pbca*, $a = 21 \cdot 041$ (5), $b = 9 \cdot 608$ (2), $c = 7 \cdot 364$ (1) Å, $Z = 4$, $D_x = 1 \cdot 267$ Mg m^{-3}. The structure is isomorphous with the pure crystals; the molecules are arranged along c, displaced by about half a molecule, to form a photopolymerizable plane-to-plane stack. Only the internal rotations about single bonds differ from those of the pure crystals, and result in considerably shorter intermolecular contacts of reactive functional groups between DSP and DSP, and somewhat longer between P2VB and P2VB when compared with those in the pure crystals. The distance between DSP and P2VB molecules is intermediate, with the functional groups no longer parallel.

Introduction. DSP and P2VB, having the same formula and approximately similar molecular dimensions, crystallize from solution isomorphously in space group *Pbca*. (DSP is dimorphic and also crystallizes in the photostable modification of $P2_1/a$.) Both materials undergo four-centre-type photopolymerization in the crystalline state yielding a linear crystalline polymer with cyclobutane rings in the main polymer chain (Hasegawa, Suzuki, Nakanishi & Nakanishi, 1973). The quantum yield of the solid-state photopolymerization differs largely, however, between these two materials (about 30 times less for P2VB than for DSP) despite the fact that both molecules behave quite similarly in the solution oligomerization (Tamaki,