References

B. A. FRENZ & ASSOCIATES INC. (1982). *DECAY. Structure Determination Package*. College Station, Texas 77840, USA.
BOND, D. R., BOURNE, S. A., NASSIMBENI, L. R. & TODA, F. (1989). *J. Crystallogr. Spectrosc. Res.* **19**, 809–822.
BOND, D. R., JOHNSON, L., NASSIMBENI, L. R. & TODA, F. (1991). *J. Solid State Chem.* **92**, 68–79.
BOURNE, S. A., NASSIMBENI, L. R. & TODA, F. (1991). *J. Chem. Soc. Perkin Trans.* 2, pp. 1335–1341.
CAIRA, M. R., NASSIMBENI, L. R. & SCHUBERT, W. D. (1991). Unpublished work.
FLYNN, J. H. & WALL, L. A. (1966). *Polymer Lett.* **4**, 323–328.
HERMAN, M. A., HOFMANS, H. & DESSEYN, H. O. (1985). *Thermochim. Acta*, **85**, 63–66.
MOTHERWELL, W. D. S. (1974). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). *SHELX86*. *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
TODA, F. (1987). *Topics in Current Chemistry*, Vol. 140, edited by E. WEBER, pp. 43–69. Heidelberg: Springer-Verlag.
TODA, F. (1988). *Topics in Current Chemistry*, Vol. 149, edited by E. WEBER, pp. 211–238. Heidelberg: Springer-Verlag.
WEBER, E. & JOSEL, H. P. (1983). *J. Incl. Phenom.* **1**, 79–85.

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Structures of Secocubane and Nortwistbrendane Derivatives

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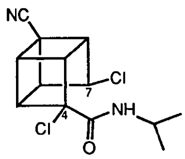
Abstract

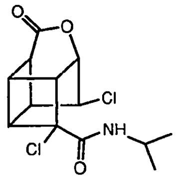
(I): 4,7-Dichloro-1-cyano-*N*-isopropyltetracyclo[4.2.0.0^{2,5}.0^{3,8}]octane-4-carboxamide, $C_{13}H_{14}Cl_2N_2O$, $M_r = 285.17$, orthorhombic, $Fdd2$, $a = 34.012$ (1), $b = 15.791$ (2), $c = 10.899$ (1) Å, $Z = 16$, $D_x = 1.29$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1.5418$ Å), $\mu = 39.2$ cm^{-1}, $F(000) = 2368$, $T = 293$ K, 1504 reflections with $I > 3\sigma(I)$, $R = 0.042$. (II): 4,7-Dichloro-*N*-isopropyl-10-oxo-9-oxatetracyclo[4.4.0.0^{2,5}.0^{3,8}]decane-4-carboxamide, $C_{13}H_{15}Cl_2NO_3$, $M_r = 304.17$, monoclinic, $P2_1/a$, $a = 9.902$ (2), $b = 9.381$ (2), $c = 15.174$ (2) Å, $\beta = 103.25$ (1)°, $Z = 4$, $D_x = 1.47$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1.5418$ Å), $\mu = 43.1$ cm^{-1}, $F(000) = 632$, 2107 reflections with $I > 3\sigma(I)$, $R = 0.036$. (I) represents the first crystallographic example of a secocubane. The nonbonded distances (C4···C7) are 2.742 (5) and 2.717 (3) Å in (I) and (II). C—C distances in the cage portions of the molecules are typical of cubanes.

Introduction

Cage compounds are of interest as potential high-density energetic materials and pharmaceutical intermediates. Selective carbon–carbon bond cleavage of substituted cubanes has led to the synthesis of polycyclic compounds such as the secocubanes and nortwistbrendanes. The detailed structures of a secocubane derivative (I)* [a preliminary report is given by Bashir-Hashemi, Dave, Ammon & Axenrod (1990)] and a nortwistbrendane derivative (II)* are reported here.



(I)



(II)

Experimental

(I) was prepared according to Bashir-Hashemi, Dave, Ammon & Axenrod (1990). (II) was prepared from the reaction of 1-(*N*,*N*-diisopropylcarboxamido)-4-cubanecarboxylic acid and HBr/acetic acid according to Eaton, Millikan & Engel (1990), followed by reaction of the lactone intermediate with thionyl chloride. Crystallographic parameters and data are given in Table 1. Enraf–Nonius CAD-4

* The IUPAC names of (I) and (II) are 4,7-dichloro-1-cyano-*N*-isopropyltetracyclo[4.2.0.0^{2,5}.0^{3,8}]octane-4-carboxamide and 4,7-dichloro-*N*-isopropyl-10-oxo-9-oxatetracyclo[4.4.0.0^{2,5}.0^{3,8}]decane-4-carboxamide.

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diffractometer with Cu source, incident-beam graphite monochromator, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å; cell parameters and crystal orientation from 25 automatically centered reflections; 2θ–θ scans over $\Delta\theta$ range of $1.5(w + 0.14\tan\theta)$; variable θ-scan speed; each scan recorded in 96 steps with two outermost 16-step intensity blocks used for background determination; diffractometer controlled with Digital Equipment Corporation MicroVAX II computer and standard Enraf–Nonius programs (version 5.0); standard reflections monitored at 1 h intervals of X-ray exposure, intensity-decay correction applied; *hkl*'s for data collection selected to maintain diffractometer χ angle in the range 0–90°, empirical absorption correction from ψ-scan data. All crystallographic calculations performed with the *TEXSAN* (Molecular Structure Corporation, 1989) program system on DEC MicroVAX II or VAX Station II computers; structures solved with the *SIR* direct-methods program (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) incorporated in *TEXSAN*. Full-matrix least-squares refinement, $\sum[w(F_o - F_c)^2]$ minimized with $w = 1/\sigma^2(F_o)$, reflections with $I < 3\sigma(I)$ excluded from refinement, corrections for secondary isotropic extinction (Zachariasen, 1968) applied; C, O, N and Cl refined with anisotropic temperature factors; H atoms initially positioned from the C-atom framework and refined with individual isotropic temperature factors; H positions in (I) not varied; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 155–175); atomic scattering factors corrected for dispersion (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 149–150).†

The preliminary publication (Bashir-Hashemi *et al.*, 1990) of the X-ray structure of (I) reported the space group as monoclinic *Cc* with $Z = 8$ (two molecules per asymmetric unit). Subsequent close examination of the two supposed crystallographically unique molecules revealed that they were for all intents and purposes perfect mirror images. In the present paper a correction has been made with a change to the orthorhombic space group *Fdd*2 with one molecule per asymmetric unit. It should be noted that the unit-cell transformation (reduction) routine in the CAD-4 diffractometer control program failed to list orthorhombic *F* as one of the possible Bravais lattices; the orthorhombic *F* lattice was indicated subsequently with the standalone *NIST*LATTICE* program (Karen & Mighell, 1991*a*). Reduction of the

† Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55245 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0416]

Table 1. *Crystallographic data for* (I) *and* (II)

	(I)	(II)
Crystal shape and dimensions (mm)	Flat triangle, 0.16 × 0.47 × 0.5	Flat hexagon, 0.06 × 0.2 × 0.3
Formula	$C_{13}H_{14}Cl_2N_2O$	$C_{13}H_{15}Cl_2NO_3$
Formula weight	285.17	304.17
Crystal system	Orthorhombic	Monoclinic
Space group	*Fdd*2 (No. 43)	$P2_1/a$ (No. 14)
Lattice parameters *a* (Å)	34.012 (3)	9.902 (2)
b (Å)	15.791 (2)	9.381 (2)
c (Å)	10.899 (1)	15.174 (2)
β (°)		103.25 (1)
V (Å^3)	5854 (1)	1372.1 (8)
Z	16	4
D_x (g cm^{-3})	1.29	1.47
F(000) (e)	2368	632
μ (cm^{-1})	39.2	43.1
Maximum 2θ (°)	118.8	139.9
No. of ψ-scan data	3	6
Transmission-factor range	0.567–1.0	0.685–1.0
No. of standard reflections measured	6	9
Standard ΔI variation (%), mean (%)	−11.8 to −1.8, −7.6	−4.0 to +1.3, −2.0
Reflection width *w* (°)	0.65	0.70
θ scan speed (° min^{-1})	0.75–8.48	0.63–8.48
Data summary		
Total No. of data measured without systematic absences	3673	2915
No. of data without standards and systematic absences	3577	2768
No. of unique data	1504*	2600
No. of data with $I > 3\sigma(I)$	1395*	2107
R_{sym} on *F* (No. of data)	0.030 (456 × 2, 539 × 4)	0.003 (168 × 2)
No. of variables	174	233
Extinction factor	0.8 (1) × 10^{-6}	0.42 (6) × 10^{-5}
R factors: *R*, *wR*, *S*	0.042, 0.059, 1.70	0.036, 0.052, 1.29
Maximum shift in final ls cycle	0.01	0.40
Min., max. in final $\Delta\rho$ map (e Å^{-3})	−0.16, 0.20	−0.22, 0.21

* Bijvoet pairs (*e.g.* I_{hkl} and I_{hk-l}) were not averaged; 1504 reflection data set contained 756 unmatched data and 374 (I_{hkl}, I_{hk-l}) pairs. R_{sym} for the 374 pairs was 0.066.

monoclinic cell [$a = 10.879$ (2), $b = 15.795$ (5), $c = 17.825$ (6) Å, $\beta = 107.69$ (2)°] gave a reduced-cell matrix (*a.a*, *b.b*, *c.c*, *b.c.*, *a.c*, *a.b*) of 91.595, 91.959, 317.731, −29.463, −29.463, −32.782, which is almost a perfect match to the ideal matrix for an orthorhombic *F* lattice. For orthorhombic *F*, the *a.b* term is equal to $a.a - 2|b.c|$; the reduced-cell parameters yield a value of −32.689 for this term. Additional confirmation for orthorhombic metric symmetry was obtained from *NIST*LATTICE* by the generation of the group of matrices, from a primitive cell derived from the *C*-centered cell, that reflect the holohedry of the lattice (Karen & Mighell, 1987; Karen & Mighell, 1991*b*); the four matrices obtained correspond to an orthorhombic lattice. The 1504 reflection data set for (I) was comprised of 1120 F_{hkl} and 374 F_{hk-l} data (374 Bijvoet pairs); least-squares refinement of the structure of (I) reported here gave *R*, *wR* and *S* factors of 0.042, 0.059 and 1.70, respectively, whereas the corresponding values for the mirror-image model were 0.054, 0.076 and 2.19. The *R*-factor ratio test (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 288–292) indicated that model (I) was superior to the enantiomer at better than the 99% confidence level.

Atomic coordinates are listed in Tables 2 and 3; bond lengths, angles and torsion angles are given in

Table 2. *Fractional coordinates, equivalent isotropic temperature factors* (Å^2) *and e.s.d.'s in parentheses for* (I)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
CL4	0.64920 (3)	0.35661 (7)	0.4977	7.15 (5)
CL7	0.49185 (3)	0.2913 (1)	0.7932 (2)	10.04 (8)
O	0.6336 (1)	0.3545 (2)	0.7966 (3)	7.4 (2)
N1	0.4531 (2)	0.3958 (5)	0.4702 (7)	13.1 (4)
N2	0.63548 (8)	0.2215 (2)	0.7277 (4)	5.6 (1)
C1	0.5232 (1)	0.3582 (3)	0.5455 (5)	6.7 (2)
C2	0.5613 (1)	0.3728 (3)	0.4770 (4)	6.0 (2)
C3	0.5772 (1)	0.2851 (2)	0.5191 (4)	5.1 (1)
C4	0.6082 (1)	0.3318 (2)	0.5962 (4)	5.4 (2)
C5	0.5806 (1)	0.4082 (2)	0.5948 (5)	6.2 (2)
C6	0.5419 (1)	0.3925 (3)	0.6666 (4)	6.7 (2)
C7	0.5392 (1)	0.3046 (3)	0.7206 (4)	6.5 (2)
C8	0.5375 (1)	0.2703 (2)	0.5924 (4)	5.8 (2)
C9	0.4836 (2)	0.3784 (5)	0.5046 (6)	9.1 (3)
C10	0.6267 (1)	0.3010 (2)	0.7166 (4)	5.3 (2)
C11	0.6562 (1)	0.1866 (3)	0.8347 (4)	6.4 (2)
C12	0.6477 (2)	0.0936 (4)	0.8488 (7)	9.3 (3)
C13	0.7001 (2)	0.2010 (5)	0.822 (1)	12.5 (5)

Table 3. *Fractional coordinates, equivalent isotropic temperature factors* (Å^2) *and e.s.d.'s in parentheses for* (II)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
CL4	0.30189 (7)	0.14504 (6)	0.84473 (5)	4.58 (3)
CL7	0.27930 (8)	0.78407 (7)	0.71343 (5)	4.88 (3)
O	0.4116 (2)	0.3001 (2)	0.6755 (1)	4.26 (7)
O9	0.4718 (2)	0.6653 (2)	0.8707 (1)	3.74 (6)
O10	0.4013 (2)	0.8037 (2)	0.9688 (1)	5.7 (1)
N	0.1790 (2)	0.2721 (2)	0.6388 (1)	3.35 (8)
C1	0.2537 (3)	0.6075 (3)	0.9031 (2)	3.50 (9)
C2	0.2971 (3)	0.4502 (3)	0.9131 (2)	3.34 (9)
C3	0.4043 (2)	0.4183 (2)	0.8539 (1)	3.06 (8)
C4	0.2940 (2)	0.3206 (2)	0.7946 (2)	3.10 (8)
C5	0.1844 (2)	0.4074 (2)	0.8288 (2)	3.16 (8)
C6	0.1794 (2)	0.5710 (3)	0.8031 (2)	3.29 (8)
C7	0.2820 (2)	0.5996 (2)	0.7455 (2)	3.15 (8)
C8	0.4235 (2)	0.5562 (2)	0.8040 (1)	3.03 (8)
C10	0.3759 (3)	0.7047 (3)	0.9181 (2)	3.9 (1)
C11	0.2987 (2)	0.2951 (2)	0.6971 (2)	3.19 (8)
C12	0.1721 (2)	0.2321 (2)	0.5445 (2)	3.16 (8)
C13	0.0355 (3)	0.2771 (4)	0.4852 (2)	4.6 (1)
C14	0.1997 (4)	0.0749 (3)	0.5376 (3)	5.2 (1)

Tables 4 and 5. The packing diagrams were put together with the *CHEMX* program (Chemical Design Ltd, 1987) on an Evans and Sutherland PS-390 graphics system. The packing coordinate files were converted to *ORTEP* format (Johnson, 1965) for the formation of preliminary drawing files. The *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display the *ORTEP* drawings on a VAX Station II monitor, label the drawings, and prepare print files for a Hewlett-Packard Laser-Jet II printer.

Discussion

ORTEP drawings of (I) and (II) are shown in Figs. 1 and 2; bond lengths, angles and torsion angles are listed in Tables 4 and 5. The Cambridge Structural Database (January 1992 update) contains no structural data for the secocubane nucleus in which the

Table 4. *Bond lengths* (Å), *angles* (°), *torsion angles* (°) *and e.s.d.'s in parentheses for* (I)

CL4—C4	1.804 (4)	C2—C5	1.545 (6)
CL7—C7	1.806 (4)	C3—C4	1.535 (5)
O—C10	1.236 (5)	C3—C8	1.586 (5)
N1—C9	1.138 (7)	C4—C5	1.529 (5)
N2—C10	1.296 (5)	C4—C10	1.536 (6)
N2—C11	1.470 (6)	C5—C6	1.551 (6)
C1—C2	1.514 (6)	C6—C7	1.510 (7)
C1—C6	1.562 (7)	C7—C8	1.499 (7)
C1—C8	1.559 (6)	C11—C12	1.505 (8)
C1—C9	1.453 (6)	C11—C13	1.516 (7)
C2—C3	1.555 (5)		
C10—N2—C11	123.2 (3)	C2—C5—C4	89.0 (3)
C2—C1—C6	90.8 (3)	C2—C5—C6	90.1 (3)
C2—C1—C8	91.7 (3)	C4—C5—C6	113.0 (3)
C2—C1—C9	127.5 (4)	C1—C6—C5	88.5 (3)
C6—C1—C8	84.5 (3)	C1—C6—C7	89.2 (3)
C6—C1—C9	124.1 (4)	C5—C6—C7	113.3 (3)
C8—C1—C9	125.9 (5)	CL7—C7—C6	109.4 (3)
C1—C2—C3	91.0 (3)	CL7—C7—C8	109.5 (3)
C1—C2—C5	90.5 (3)	C6—C7—C8	88.4 (3)
C3—C2—C5	86.0 (3)	C1—C8—C3	88.2 (3)
C2—C3—C4	88.4 (3)	C1—C8—C7	89.7 (3)
C2—C3—C8	89.1 (3)	C3—C8—C7	112.6 (3)
C4—C3—C8	112.2 (3)	N1—C9—C1	178.0 (8)
CL4—C4—C3	108.0 (3)	O—C10—N2	123.6 (4)
CL4—C4—C5	107.3 (3)	O—C10—C4	117.6 (3)
CL4—C4—C10	105.1 (2)	N2—C10—C4	118.8 (3)
C3—C4—C5	87.3 (3)	N2—C11—C12	110.7 (4)
C3—C4—C10	126.7 (3)	N2—C11—C13	110.2 (5)
C5—C4—C10	120.7 (3)	C12—C11—C13	110.3 (5)
CL4—C4—C3—C2	−84.5 (3)	C1—C8—C3—C4	88.7 (4)
CL4—C4—C3—C8	−172.9 (2)	C1—C8—C7—C6	−21.9 (3)
CL4—C4—C5—C2	85.0 (3)	C2—C1—C6—C5	0.7 (3)
CL4—C4—C5—C6	174.8 (3)	C2—C1—C6—C7	−112.6 (3)
CL4—C4—C10—O	90.3 (4)	C2—C1—C8—C3	−0.8 (3)
CL4—C4—C10—N2	−87.5 (3)	C2—C1—C8—C7	111.9 (3)
CL7—C7—C6—C1	−88.3 (3)	C2—C3—C4—C5	22.8 (3)
CL7—C7—C6—C5	−176.3 (3)	C2—C3—C4—C10	149.8 (3)
CL7—C7—C8—C1	88.2 (3)	C2—C3—C8—C7	−88.2 (4)
CL7—C7—C8—C3	176.1 (3)	C2—C5—C4—C3	−23.0 (3)
O—C10—N2—C11	−2.8 (6)	C2—C5—C4—C10	−154.9 (3)
O—C10—C4—C3	−142.9 (4)	C2—C5—C6—C7	87.8 (4)
O—C10—C4—C5	−30.9 (5)	C3—C2—C1—C6	85.3 (3)
N1—C9—C1—C2	−20 (21)	C3—C2—C1—C8	0.8 (3)
N1—C9—C1—C6	103 (21)	C3—C2—C1—C9	−138.8 (6)
N1—C9—C1—C8	−147 (21)	C3—C2—C5—C4	22.7 (3)
N2—C10—C4—C3	39.4 (5)	C3—C2—C5—C6	−90.2 (3)
N2—C10—C4—C5	151.3 (3)	C3—C4—C5—C6	66.7 (4)
C1—C2—C3—C4	−113.0 (3)	C3—C8—C1—C6	−91.5 (3)
C1—C2—C3—C8	−0.8 (3)	C3—C8—C1—C9	139.9 (5)
C1—C2—C5—C4	113.7 (3)	C3—C8—C7—C6	66.1 (3)
C1—C2—C5—C6	0.7 (3)	C4—C3—C2—C5	−22.6 (3)
C1—C6—C5—C2	−0.7 (3)	C4—C3—C8—C7	−0.2 (4)
C1—C6—C5—C4	−89.7 (4)	C4—C5—C6—C7	−1.2 (5)
C1—C6—C7—C8	21.8 (3)	C4—C10—N2—C11	174.8 (3)
C1—C8—C3—C2	0.8 (3)	C5—C2—C1—C6	−0.7 (3)
C5—C2—C1—C8	−85.2 (3)		
C5—C2—C1—C9	135.2 (6)	C6—C5—C4—C10	−65.2 (4)
C5—C2—C3—C8	89.6 (3)	C7—C6—C1—C8	−21.0 (3)
C5—C4—C3—C8	−65.6 (3)	C7—C6—C1—C9	109.2 (5)
C5—C6—C1—C8	92.3 (3)	C7—C8—C1—C9	−107.5 (5)
C5—C6—C1—C9	−137.5 (5)	C8—C3—C4—C10	61.4 (4)
C5—C6—C7—C8	−66.2 (4)	C10—N2—C11—C12	156.2 (4)
C6—C1—C8—C7	21.2 (3)	C10—N2—C11—C13	−81.5 (6)

two unlinked carbon atoms (C4 and C7) are not bridged by one or two atoms. Homocubane examples, in which there is a one atom bridge, show nonbonded distances analogous to C4···C7 of 2.27 Å [1,4-dibromohomocubane ethylene ketal (Watson, Kashyap, Marchand & Vidyasagar, 1989); 6,6-ethylenedioxyheptachloropentacyclo[5.2.0.0^{2,5}.0^{3,9}.0^{4,8}]-nonane-3-carboxylic acid (Okaya, 1969)], and the range is 2.52–2.68 Å for compounds [*trans*-9,10-pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decanedicarboxylic acid (Schaefer & Walthers, 1971); basketene photo-

Table 5. *Bond lengths* (Å), *angles* (°), *torsion angles* (°) *and e.s.d.'s in parentheses for* (II)

CL4—C4	1.809 (2)	C2—C5	1.545 (3)
CL7—C7	1.796 (2)	C2—C3	1.569 (3)
O—C11	1.236 (3)	C3—C8	1.533 (3)
O9—C10	1.367 (3)	C3—C4	1.547 (3)
O9—C8	1.442 (3)	C4—C11	1.509 (3)
O10—C10	1.196 (3)	C4—C5	1.540 (3)
N—C11	1.324 (3)	C5—C6	1.582 (3)
N—C12	1.466 (3)	C6—C7	1.508 (3)
C1—C10	1.490 (4)	C7—C8	1.532 (3)
C1—C2	1.535 (3)	C12—C13	1.504 (4)
C1—C6	1.566 (3)	C12—C14	1.508 (4)
C10—O9—C8	113.8 (2)	C2—C5—C6	85.9 (2)
C11—N—C12	121.9 (2)	C7—C6—C1	107.1 (2)
C10—C1—C2	112.0 (2)	C7—C6—C5	109.2 (2)
C10—C1—C6	117.8 (2)	C1—C6—C5	89.5 (2)
C2—C1—C6	86.8 (2)	C6—C7—C8	105.4 (2)
C1—C2—C5	92.0 (2)	C6—C7—CL7	111.0 (2)
C1—C2—C3	109.8 (2)	C8—C7—CL7	111.6 (2)
C5—C2—C3	86.1 (2)	O9—C8—C7	109.3 (2)
C8—C3—C4	111.3 (2)	O9—C8—C3	108.1 (2)
C8—C3—C2	107.4 (2)	C7—C8—C3	108.1 (2)
C4—C3—C2	88.0 (2)	O10—C10—O9	118.6 (2)
C11—C4—C5	126.7 (2)	O10—C10—C1	128.1 (3)
C11—C4—C3	119.2 (2)	O9—C10—C1	113.1 (2)
C11—C4—CL4	105.1 (1)	O—C11—N	123.7 (2)
C5—C4—C3	87.1 (2)	O—C11—C4	119.1 (2)
C5—C4—CL4	107.8 (2)	N—C11—C4	117.2 (2)
C3—C4—CL4	109.7 (2)	N—C12—C13	110.3 (2)
C4—C5—C2	89.2 (2)	N—C12—C14	110.4 (2)
C4—C5—C6	114.5 (2)	C13—C12—C14	112.7 (3)
CL4—C4—C11—O	94.4 (2)	C1—C2—C3—C8	2.0 (2)
CL4—C4—C11—N	−87.3 (2)	C1—C2—C3—C4	113.8 (2)
CL4—C4—C5—C2	−86.3 (2)	C1—C6—C7—C8	−36.0 (2)
CL4—C4—C5—C6	−171.4 (2)	C1—C6—C5—C4	105.0 (2)
CL4—C4—C3—C8	−167.3 (1)	C1—C6—C5—C2	17.8 (2)
CL4—C4—C3—C2	84.8 (2)	C2—C1—C6—C7	92.1 (2)
CL7—C7—C6—C1	84.9 (2)	C2—C1—C6—C5	−17.9 (2)
CL7—C7—C6—C5	−179.5 (2)	C2—C5—C4—C11	148.2 (2)
CL7—C7—C8—O9	−43.9 (2)	C2—C5—C4—C3	23.5 (2)
CL7—C7—C8—C3	−161.3 (1)	C2—C5—C6—C7	−90.1 (2)
O—C11—N—C12	−8.0 (4)	C2—C3—C8—C7	59.5 (2)
O—C11—C4—C5	−139.1 (2)	C2—C3—C4—C11	−154.1 (2)
O—C11—C4—C3	−29.0 (3)	C2—C3—C4—C5	−23.1 (2)
O9—C10—C1—C2	−48.4 (3)	C3—C8—O9—C10	67.2 (2)
O9—C10—C1—C6	49.9 (3)	C3—C8—C7—C6	−40.7 (2)
O9—C8—C7—C6	76.7 (2)	C3—C4—C5—C6	−61.6 (2)
O9—C8—C3—C4	−153.5 (2)	C3—C2—C1—C10	50.6 (3)
O9—C8—C3—C2	−58.7 (2)	C3—C2—C1—C6	−68.2 (2)
O10—C10—O9—C8	173.0 (2)	C3—C2—C5—C4	−23.1 (2)
O10—C10—C1—C2	127.1 (3)	C3—C2—C5—C6	91.5 (2)
O10—C10—C1—C6	−134.6 (3)	C4—C11—N—C12	173.8 (2)
N—C11—C4—C5	39.2 (3)	C4—C5—C6—C7	−2.9 (3)
N—C11—C4—C3	149.3 (2)	C4—C3—C8—C7	−35.3 (2)
C1—C10—O9—C8	−11.1 (3)	C4—C3—C2—C5	23.0 (2)
C1—C2—C5—C4	−132.8 (2)	C5—C2—C1—C6	18.4 (2)
C1—C2—C5—C6	−18.2 (2)	C5—C2—C1—C10	137.2 (2)
C5—C2—C3—C8	−88.7 (2)	C7—C6—C1—C10	−21.1 (3)
C5—C4—C3—C8	84.8 (2)	C7—C8—O9—C10	−50.2 (2)
C5—C6—C7—C8	59.6 (2)	C8—C3—C4—C11	−46.2 (3)
C5—C6—C1—C10	−131.1 (2)	C11—N—C12—C13	154.0 (2)
C6—C5—C4—C11	63.1 (3)	C11—N—C12—C14	−80.8 (3)

dimer (Jones, Deadman & LeGoff, 1973); 7,8-diazapentacyclo[4.2.2.0^{2,5}.0^{3,9}.0^{4,10}]dec-7-ene (Ottersen, Romming & Snyder, 1976)] with a two-atom bridge. In the absence of bridging atoms which force C4 and C7 together, the distances are larger at 2.742 (5) and 2.717 (3) Å in (I) and (II), respectively. The 2.717 Å distance in (II) is similar to the 2.708 Å value found in 4-methoxycarbonyl-7-bromo-10-oxo-9-oxatetracyclo[4.4.0.0^{2,5}.0^{3,8}]decane (Eaton, Millikan & Engel, 1990).

In the cage portions of (I) and (II), the carbon–carbon distances not associated with atoms C1, C4 and C7 in (I) and with atoms C1, C4, C7 and C8 in (II) range from a low of 1.533 Å [bond C4—C5 in (II)] to a high of 1.586 Å [bond C3—C8 in (I)] and are characteristic of the values found in cubanes. It is interesting that the longest C—C bonds, C3—C8 = 1.586 (5) Å in (I) and C5—C6 = 1.582 (3) Å in (II), are in similar locations in the two structures. The bond distances in the cage associated with C4 and C7 distances average 1.525 (5) Å. The other bond lengths and angles have typical values. The relative orientations of the cages and amide substituents are very similar. For example, the O—C10—C4—C3 and O—C10—C4—C5 dihedral angles in (I) are

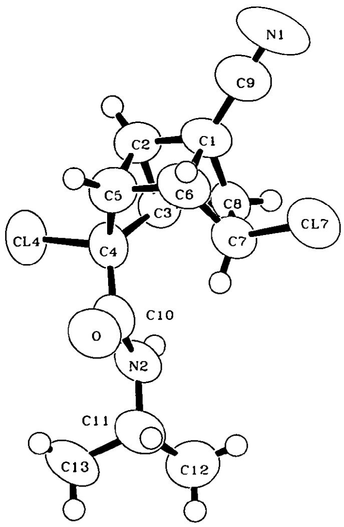

Fig. 1. *ORTEP* drawing of (I). The C, O, N and Cl atoms are shown as 50% ellipsoids, and the H atoms are depicted as spheres with $B = 1.5$ Å^2.

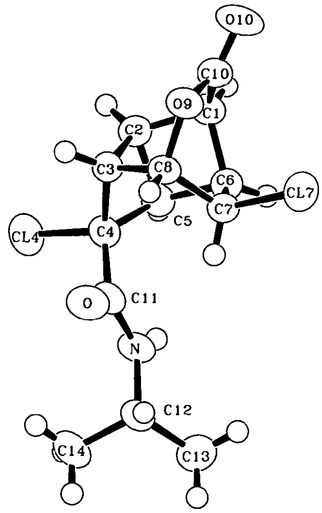

Fig. 2. *ORTEP* drawing of (II). The C, O, N and Cl atoms are shown as 50% ellipsoids, and the H atoms are depicted as spheres with $B = 1.5$ Å^2.

−142.9 (4) and −30.9 (5)°, and the corresponding angles for O—C11—C4—C5 and O—C11—C4—C3 in (II) are −139.1 (2) and −29.0 (3)°.

Packing diagrams are given in Figs. 3 and 4. N—H···O=C interactions between molecules related by glide-plane symmetry produce the closest intermolecular distances in both structures. In (I), the molecules are related by a glide parallel to the *bc* diagonal while in (II) the molecules are linked by an *a* glide. The H—N—C=O moieties are close to and approximately parallel to the glide planes in both structures. This permits a close approach of the C=O and H—N portions of glide-related molecules and places the hydrocarbon portions of the molecules on opposite sides of the planes. The interaction is stronger in (I) with O···H = 1.85 and O···N2 = 2.780 (4) Å than (II) with O···H = 2.13 and O···N = 2.908 (3) Å. Angles associated with the C=O···H—N interactions are C10—O···H = 157.0 and C10—O···N2 = 155.7 (3)° in (I) and C11—O···H = 161.6 (7) and C11—O···N = 163.9 (2)° in (II). In view of the similarity between these angles, other nonbonded interactions in (II) are probably responsible for limiting the close approach of hydrogen-bonded molecules in (II) to a distance comparable to that in (I).

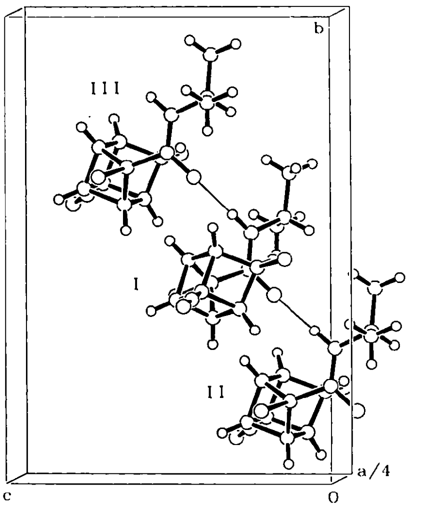

Fig. 3. *ORTEP* ball-and-stick packing diagram for (I). The molecules designated as (I), (II) and (III) are at *x*, *y*, *z*; $\frac{1}{4} - x$, $-\frac{1}{4} + y$, $-\frac{1}{4} + z$; and $\frac{1}{4} - x$, $\frac{1}{4} + y$, $\frac{1}{4} + z$. The indicated O···H intermolecular distance is 1.85 Å.

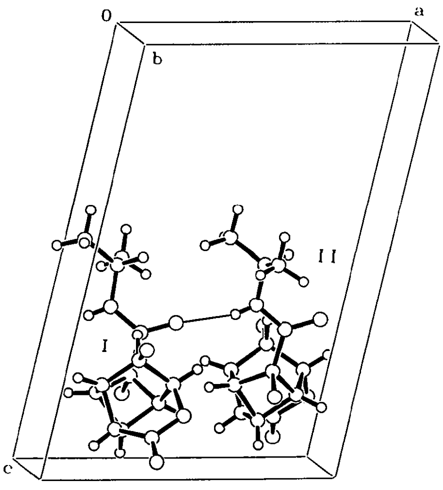

Fig. 4. *ORTEP* ball-and-stick packing diagram for (II). Molecules (I) and (II) are at *x*, *y*, *z* and $\frac{1}{2} + x$, $\frac{1}{2} - y$, *z*. The single O···H intermolecular contact indicated is 2.13 Å.

The *SVDHA* program (Zhang, 1985) was used to calculate the molecular volumes of (I) and (II) with van der Waals radii for C, H, N, O and Cl of 1.70, 1.10, 1.55, 1.52 and 1.75 Å, respectively (C—H and N—H bonds were adjusted to 1.098 and 1.030 Å). The packing coefficients [efficiencies, PC = (molecular volume/unit-cell volume per molecule) (Kitaigorodskii, 1961)] are 0.614 and 0.674 for (I) and (II) and indicate that crystal packing is less efficient in the former and this may be responsible for the larger atomic displacement parameters in (I).

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References

Bashir-Hashemi, A., Dave, P. R., Ammon, H. L. & Axenrod, T. (1990). *Tetrahedron Lett.* **31**, 4835–4836.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Chemical Design Ltd (1987). *CHEMX. The CHEMX Reference Manual.* Chemical Design Ltd, Oxford, England.

Eaton, P. E., Millikan, R. & Engel, P. (1990). *J. Org. Chem.* **55**, 2823–2826.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Jones, N. J., Deadman, D. & LeGoff, E. (1973). *Tetrahedron Lett.* **14**, 2087–2088.

Karen, V. L. & Mighell, A. D. (1987). *Acta Cryst.* A**43**, 375–384.

Karen, V. L. & Mighell, A. D. (1991*a*). *NIST*LATTICE. A Program to Analyze Lattice Relationships.* Technical Note 1290. National Institute of Standards and Technology, Gaithersburg, Maryland, USA.

Karen, V. L. & Mighell, A. D. (1991*b*). *J. Appl. Cryst.* **24**, 1076–1078.

Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography.* New York: Consultants Bureau.

Luo, J., Ammon, H. L. & Gilliland, G. J. (1989). *J. Appl. Cryst.* **22**, 186.

Molecular Structure Corporation (1989). *TEXSAN. Single-Crystal Structure Analysis Software*. Version 5. Molecular Structure Corporation, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
OKAYA, Y. (1969). *Acta Cryst.* **B25**, 1882–1889.
OTTERSEN, T., ROMMING, C. & SNYDER, J. P. (1976). *Acta Chem. Scand. Ser. B*, **30**, 407–416.
SCHAEFER, J. P. & WALTHERS, K. K. (1971). *Tetrahedron*, **27**, 5281–5287.
WATSON, W. H., KASHYAP, R. P., MARCHAND, A. P. & VIDYASAGAR, V. (1989). *Acta Cryst.* **C45**, 2010–2012.
ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212–216.
ZHANG, D. (1985). *SVDHA*. Program to calculate molecular volume, area and accessible surface area. Unpublished.

Acta Cryst. (1992). **B48**, 837–848

Charge Density Studies on Small Organic Molecules Around 20 K: Oxalic Acid Dihydrate at 15 K and Acetamide at 23 K

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Abstract

High-resolution X-ray diffraction data were collected for oxalic acid dihydrate at 15 K and for acetamide at 23 K (and at 100 K for comparison) to obtain accurate crystal data and experimental electron density. The measurements were performed with a large full-circle Eulerian cradle (400 mm diameter) with an offset χ circle equipped with a double-stage He refrigerator (Displex DE 202) and a Be vacuum chamber around the cold head. Conventional and multipole refinements were carried out on the data. Deformation density maps were generated by $X-X$ Fourier syntheses and compared with the static distribution obtained from the multipole model. Results are also compared with those reported previously. The change in the resolution of the deformation density due to the improved accuracy of the high-order data is analyzed. For the acetamide molecule the temperature dependence of the measured intensities and the thermal parameters are also examined.

Introduction

In order to obtain accurate molecular data and static electronic properties from X-ray diffraction observations the vibrational smearing of the electron density due to atomic motion should be properly decomposed from the asphericity due to chemical bonds. In any scattering formalism applicable for this task the parameters accounting for the two effects are expected to be strongly correlated. Reflections detected at low scattering angles carry information about the diffuse characteristics of the electron density, while high-order data are mainly affected by the sharp features of the distribution near to the nucleus. The number of observable intensity data for a given crystal and experimental conditions is limited. One way to increase the resolution of the diffraction data at high scattering angles is to decrease the temperature and so the delocalization of the electron density caused by vibrational smearing. This is why the experiment should be carried out at the lowest temperature feasible for a single-crystal diffractometer.

For neutron scattering, temperatures of around 20 K have been realized for more than ten years (Allibon, Filhol, Lehmann, Mason & Simms, 1981) and a number of neutron structure determinations at this very low temperature have been reported (Jeffrey, Ruble, McMullan, De Frees, Binkley & Pople, 1980; Jeffrey, Ruble & Yates, 1983, and papers cited therein; Weber, Craven, Sawzik & McMullan, 1991). Although cryostats for this temperature have also been mounted on X-ray diffractometers in a few cases (Hendriksen, Larsen & Rasmussen, 1986), most single-crystal X-ray data sets are still collected around 100 K using conventional nitrogen gas stream devices. The advantages of neutron data at 20 K cannot be utilized unless the corresponding X-ray data are available. One of the few exceptions is reported by Coppens & Lehmann (1976), who carried out a charge-density study at 30 K using a liquid-helium cooling device.

Based on our earlier experiences with a single-stage cryostat at 50 K (Zobel & Luger, 1990) we

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