In Y_3Co and Y_8Co_5 the trigonal prisms are tilted with respect to each other as in FeB, while in Y_3Co_2 and Y_4Co_3 the prism base planes are parallel as in CrB. In Y_3Co_2 and Y_4Co_3 infinite columns of prisms are formed. The change occurring from one framework to another is the side by side arrangement of the columns.

With the use of the concept of the trigonal prism linkage coefficient, it is possible to relate the stoichiometry of this type of compound to the linkage of prisms in the crystal structure. Moreover in certain cases it should be possible to predict the way the prisms are joined together from the knowledge of the composition of the alloy.

The assistance of Dr H. D. Flack with the computer programming is acknowledged.

Fig. 3. Projection of structural units of prisms in Y_3Co, Y_3Co_2 and Y_4Co_3. The number near each corner indicates the number of lower and upper prisms which share this corner.

References

BUSCHOW, K. H. J. (1971). Philips Res. Rep. 26, 49–64.

BUSCHOW, K. H. J. & VAN DER GOOT, A. S. (1969). J. Less-Common Met. 18, 309–311.

CROMER, C. & MANN, J. (1968). Acta Cryst. A24, 321–324.

FLACK, H. D. (1974a). Supplement to X-RAY System 1972, Laboratoire de Cristallographie aux Rayons X, Université de Genève, Geneva, Switzerland.

FLACK, H. D. (1974b). Acta Cryst. A30, 569–573.

FLACK, H. D. (1975). J. Appl. Cryst. 8, 520–521.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press.

LEMAIRE, R., SCHWEIZER, J. & YAKINTHOS, J. (1969). Acta Cryst. B25, 710–713.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1972). LSAM, a System of Computer Programs for the Automatic Solution of Centrosymmetric Crystal Structures. Department of Physics, Univ. of York, York (England).

MOREAU, J. M., PACCARD, D. & PARTHÉ, E. (1974). Acta Cryst. B30, 2583–2586.

MOREAU, J. M., PARTHÉ, E. & PACCARD, D. (1975). Acta Cryst. B31, 747–749.

PARTHÉ, E. (1970). Les Eléments des Terres Rares, Colloques Internationaux de Centre National de la Recherce Scientifique, No. 180, pp. 61–79. Paris: CNRS.

RAY, A. E. (1974). Cobalt, 1, 13–20.

STRNAT, K. J., OSTERTAG, W., ADAMS, N. J. & OLSON, J. C. (1965). Proceedings of Fifth Rare-Earth Research Conference, Ames, Iowa, Vol. 5, p. 67.

X-RAY System (1972) Version of June. Technical Report TR-192 of the Computer Science Center, Univ. of Maryland, U.S.A.

YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1975). A Fortran IV Program for the Intensity Calculation of Powder Patterns, 1975 Version, Laboratoire de Cristallographie aux Rayons X, Université de Genève, Geneva, Switzerland.

The Carvoxime System. I. X-ray Study of dl-Carvoxime (m.p. 92°C)

By H. A. J. OONK AND J. KROON

Laboratoria voor Structuurchemie en Chemische Thermodynamica, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands

dl-Carvoxime, $C_{10}H_{15}NO$, (m.p. 92°C) is monoclinic $P2_1/c$, with $a=9.856$ (3), $b=11.848$ (3), $c=8.480$ (3) Å, $\beta=98.95$ (5)°, $Z=4$. The structure was determined from 1767 independent intensities measured with Mo $K\alpha$ radiation on an automatic four-circle diffractometer and refined by a block-diagonal least-squares procedure to $R=0.057$. Contrary to previous expectations there is no substitutional disorder. In the crystal structure hydrogen bonding in which six-membered rings occur is found.

Introduction

Ever since its determination (Adriani, 1900) the phase diagram of the solid–liquid equilibrium in the system d-carvoxime + l-carvoxime has played a controversial role. The diagram, which is of type II according to Roo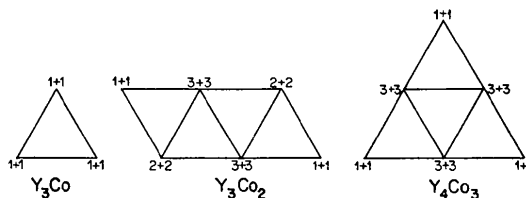zeboom's (1891, 1899) classification, suggests a continuous series of mixed crystals in which the 1:1 (the dl) composition, has the highest melting point. The possibility of such a type of phase diagram in a system of optical antipodes was excluded by Van Laar (1908) on thermodynamic grounds, which, however,

started from an extension of the van der Waals equation of state to liquid and solid solutions.

The idea of a continuous series of mixed crystals was strengthened by crystallographic observations on *d*- (or *l*-) and *dl*-carvoxime. Beyer (1891) found a great similarity in axial ratios, and Oonk (1965) reported a pronounced similarity in the intensities of X-ray reflexions from *d*- and *dl*-carvoxime. These observations, with the equality of the entropies of melting (Tammann, 1914), seemed to point to a structure of *dl*-carvoxime in which the *d*- and *l*-molecules are randomly distributed. The geometrical similarity between the *d*- and the *l*-molecules, required for a continuous series of mixed crystals of the substitutional type, pointed to planar molecules in which the isopropenyl group is equatorially attached to the asymmetric C atom of the cyclohexene ring.
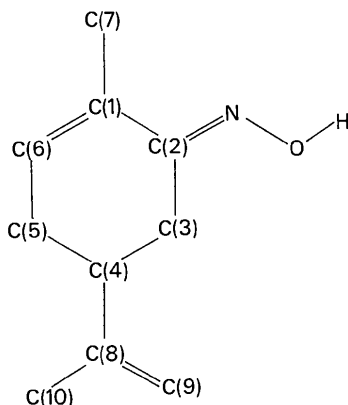
The first indications for the untenability of the solid-solution model came from a redetermination of the entropies of melting (Jacques, 1970): the entropy of melting of *d*-carvoxime, m.p. 72 °C, and that of *dl*-carvoxime, m.p. 92 °C, are in the ratio of about 2:3. These observations imply that *dl*-carvoxime has to be considered a much less disordered structure than was believed in 1965.

We thus decided to make a closer study of the structural and thermodynamic properties of the carvoxime system. The present communication reports the structure of *dl*-carvoxime.

After completion of the determination we found that the structure had already been reported elsewhere (Baert & Fouret, 1975). In spite of this it seems worth while to present our results because differences are found between the two determinations concerning chemical formula, cell parameters and atomic coordinates.

Experimental

Crystal data

Transparent plate-like crystals were obtained by evaporation from methanol. $C_{10}H_{15}NO$, M.W. 165·23. Space group $P2_1/c$; $a=9·856$ (3), $b=11·848$ (3), $c=8·480$ (3) Å, $\beta=98·95$ (5)°; $Z=4$, $V=978·2$ Å^3, $D_x=1·122$, $D_m=1·126$ g cm^{-3}, $\mu(Mo)=0·84$ cm^{-1}.

All X-ray measurements were made on an automatic four-circle diffractometer with Zr-filtered Mo radiation. Cell dimensions were determined by measurement of the θ, φ and χ values of six reflexions [there

Fig. 1. Key to the numbering of the atoms in the carvoxime molecule.

Table 1. *Atomic parameters*

The e.s.d.'s are in parentheses.

(*a*) Heavy atoms. Fractional parameters are $\times 10^4$. The thermal parameters are in the form $T=\exp\left[-\frac{2\pi^2}{100}\sum\limits_{i=1}^{3}\sum\limits_{j=1}^{3}U_{ij}h_ih_ja_i^*a_j^*\right]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	6636 (1)	4716 (1)	5441 (2)	5·67 (8)	4·74 (8)	10·08 (12)	0·69 (7)	0·49 (8)	−0·38 (8)
N	5688 (2)	3907 (1)	4719 (2)	5·21 (10)	5·19 (10)	6·95 (12)	0·73 (8)	0·61 (8)	0·15 (9)
C(1)	5318 (2)	2028 (2)	3914 (2)	4·72 (12)	5·87 (13)	5·38 (14)	0·60 (10)	−0·12 (10)	−0·07 (11)
C(2)	6202 (2)	2910 (2)	4722 (2)	4·67 (11)	4·98 (12)	5·13 (14)	0·84 (9)	0·77 (10)	0·39 (10)
C(3)	7647 (2)	2617 (2)	5452 (2)	4·62 (12)	5·11 (12)	6·54 (15)	0·60 (10)	0·15 (10)	−0·28 (11)
C(4)	7776 (2)	1403 (2)	6014 (2)	4·86 (12)	5·03 (13)	6·25 (14)	1·12 (9)	−0·14 (10)	−0·31 (10)
C(5)	7189 (2)	611 (2)	4682 (3)	5·96 (13)	5·10 (13)	7·04 (15)	0·76 (10)	−0·02 (12)	−0·64 (11)
C(6)	5800 (2)	984 (2)	3870 (2)	5·55 (13)	6·26 (14)	6·07 (15)	−0·03 (11)	−0·30 (11)	−1·07 (11)
C(7)	3912 (2)	2347 (2)	3073 (3)	5·89 (14)	8·23 (17)	8·18 (18)	0·74 (12)	−1·05 (13)	−0·29 (13)
C(8)	9217 (2)	1074 (2)	6772 (3)	5·43 (13)	5·63 (13)	7·53 (16)	1·60 (11)	−0·42 (11)	−1·23 (12)
C(9)	10305 (2)	1681 (2)	6621 (4)	5·62 (16)	7·42 (18)	23·06 (39)	1·40 (13)	−2·85 (20)	−0·94 (20)
C(10)	9322 (3)	4 (2)	7668 (3)	8·00 (18)	13·76 (25)	9·57 (21)	3·99 (16)	−0·36 (15)	2·66 (18)

(*b*) H atoms. Fractional parameters are $\times 10^3$.

	x	y	z	B(Å^2)		x	y	z	B(Å^2)
H(O)	610 (2)	527 (1)	554 (2)	6·3	H′(C7)	347 (2)	172 (1)	248 (2)	7·6
H(C3)	797 (2)	310 (1)	633 (2)	6·3	H″(C7)	335 (2)	259 (1)	379 (2)	7·6
H′(C3)	826 (2)	275 (1)	456 (2)	6·3	H(C9)	1034 (2)	241 (2)	616 (2)	10·1
H(C4)	715 (2)	130 (1)	693 (2)	6·3	H′(C9)	1108 (2)	142 (2)	713 (2)	10·1
H(C5)	715 (2)	−12 (1)	506 (2)	6·3	H(C10)	861 (2)	−5 (2)	851 (2)	10·1
H′(C5)	784 (2)	60 (1)	380 (2)	6·3	H′(C10)	1022 (2)	−5 (2)	829 (2)	10·1
H(C6)	526 (2)	41 (1)	322 (2)	6·3	H″(C10)	921 (2)	−68 (2)	674 (2)	10·1
H(C7)	397 (2)	294 (1)	232 (2)	7·6					

are differences of up to 0·05 Å from the data given by Baert & Fouret (1975)]. The crystal fragment used was 0·75 × 0·60 × 0·30 mm.

Intensity data

The intensities were measured by the ω scan method with a scan width of $(1 + 0·8\ \mathrm{tg}\ \theta)°$. For each reflexion the scan speed was adjusted in order to obtain a minimum of 1000 counts, provided that the scan time did not exceed 60 s. The time allotted to the measurement of the background was half that of the peak. Within the sphere of reflexion limited at $\sin\theta/\lambda = 0·65$, 8738 reflexions were measured. Intensities for equivalent reflexions of the type hkl, $h\bar{k}l$, $h\bar{k}l$ and $\bar{h}kl$

Table 2. *Observed and calculated structure factors*

The columns list h, $|F_o|$ and F_c. Reflexions marked with an asterisk have $I < 2·5\sigma(I)$ and were excluded from refinement.

Table 2 (cont.)

[Dense numerical structure-factor table — columns of h, k, l with observed and calculated structure factors; individual values not legibly reproducible.]

were averaged and their statistical standard deviation reduced accordingly. Of the 2245 independent reflexions 1767 had $I > 2 \cdot 5\sigma(I)$ and were used for the structure determination. The data were corrected for the LP factor but not for absorption.

Structure determination

All calculations were performed with a version of the X-RAY System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) extended and implemented by the Dutch X-RAY System Group. The structure was solved with *MULTAN* (Main, Woolfson & Germain,

Fig. 2. Projection of the structure along b. Of the H atoms only that of the oxime group is depicted.

1971). All H atoms were located from a difference synthesis. Scattering factors for O, N and C were taken from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). After block-diagonal least-squares refinement $[w^{-1} = \sigma^2(F)]$ of coordinates and the heavy-atom anisotropic thermal parameters R was $0 \cdot 057$ ($R_w = 0 \cdot 046$). The isotropic temperature factor of each H atom was kept constant at the value corresponding to that of the atom to which it is attached. The ratio of largest shift in the last cycle to standard deviation amounts to $0 \cdot 6$ for the heavy and to $1 \cdot 0$ for the H atoms. The final parameters are in Table 1. Observed and calculated structure factors are in Table 2.

Discussion of the structure

The geometry of the molecule can be inferred from Fig. 1 and Table 3. The isopropenyl group is equatorially attached to the cyclohexene ring, as was expected; it exhibits very high thermal motion. Nevertheless there is no rotational disorder of the H atoms of the methyl group. The same holds for the methyl group at the 1 position. In view of the scope of the present investigation it is important to note that positional disorder in the structure of this crystal is out of the question. Fig. 2 shows the projection of the structure down b. The oxime group H atom [overlooked by Baert & Fouret (1975)] is involved in hydrogen bonding ($r_{O \cdots N}$ = 2·798 Å): d- and l-molecules form dimers by hydrogen bonding across the centre of symmetry. This kind of hydrogen bonding in which six-membered rings occur which are planar within experimental error, is shown in Fig. 3. It is noteworthy that the geometry of the H-bonded system is very like that of the most stable H-bonded dimers $(NH_2OH)_2$ found by

Table 3. *Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses*

N—O	1·410 (2)	O—N—C(2)	112·9 (1)
C(2)–N	1·286 (2)	N—C(2)–C(1)	116·8 (2)
C(1)–C(2)	1·460 (3)	N—C(2)–C(3)	124·1 (2)
C(2)–C(3)	1·503 (3)	C(1)–C(2)–C(3)	119·1 (2)
C(3)–C(4)	1·514 (3)	C(2)–C(3)–C(4)	112·1 (2)
C(4)–C(5)	1·513 (3)	C(3)–C(4)–C(5)	110·5 (2)
C(5)–C(6)	1·501 (3)	C(4)–C(5)–C(6)	112·1 (2)
C(1)–C(7)	1·505 (3)	C(5)–C(6)–C(1)	124·5 (2)
C(4)–C(8)	1·515 (3)	C(6)–C(1)–C(2)	119·4 (2)
C(8)–C(9)	1·314 (3)	C(6)–C(1)–C(7)	121·8 (2)
C(8)–C(10)	1·474 (4)	C(2)–C(1)–C(7)	118·7 (2)
		C(3)–C(4)–C(8)	113·9 (2)
		C(5)–C(4)–C(8)	112·4 (2)
		C(4)–C(8)–C(9)	122·9 (2)
		C(4)–C(8)–C(10)	115·2 (2)
		C(9)–C(8)–C(10)	121·8 (2)

O—H(O)	0·85 (2)	C(7)—H'(C7)	0·96 (2)
C(3)–H(C3)	0·95 (2)	C(7)—H''(C7)	0·93 (2)
C(3)–H'(C3)	1·05 (2)	C(9)—H(C9)	0·95 (2)
C(4)–H(C4)	1·07 (2)	C(9)—H'(C9)	0·87 (2)
C(5)–H(C5)	0·93 (2)	C(10)-H(C10)	1·07 (2)
C(5)–H'(C5)	1·06 (2)	C(10)-H'(C10)	0·96 (2)
C(6)–H(C6)	0·98 (2)	C(10)-H''(C10)	1·12 (2)
C(7)–H(C7)	0·96 (2)		

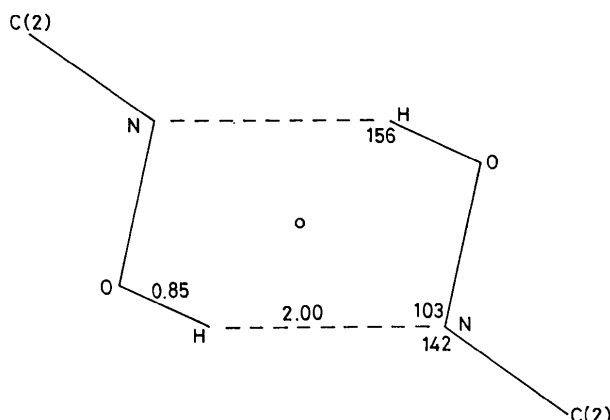|	
H(O)—O—N	101 (1)
H(C3)—C(3)—C(2)	111 (1)
H(C3)—C(3)—C(4)	109 (1)
H(C3)—C(3)—H'(C3)	108 (1)
H'(C3)—C(3)—C(2)	106 (1)
H'(C3)—C(3)—C(4)	110 (1)
H(C4)—C(4)—C(3)	108 (1)
H(C4)—C(4)—C(5)	106 (1)
H(C4)—C(4)—C(8)	106 (1)
H(C5)—C(5)—C(4)	111 (1)
H(C5)—C(5)—C(6)	110 (1)
H(C5)—C(5)—H'(C5)	107 (1)
H'(C5)—C(5)—C(4)	109 (1)
H'(C5)—C(5)—C(6)	107 (1)
H(C6)—C(6)—C(5)	116 (1)
H(C6)—C(6)—C(1)	120 (1)
H(C7)—C(7)—C(1)	111 (1)
H(C7)—C(7)—H'(C7)	107 (1)
H(C7)—C(7)—H''(C7)	108 (2)
H'(C7)—C(7)—C(1)	111 (1)
H'(C7)—C(7)—H''(C7)	109 (2)
H''(C7)—C(7)—C(1)	111 (1)
H(C9)—C(9)—C(8)	128 (1)
H(C9)—C(9)—H'(C9)	116 (2)
H'(C9)—C(9)—C(8)	115 (1)
H(C10)—C(10)-C(8)	113 (1)
H(C10)—C(10)-H'(C10)	106 (2)
H(C10)—C(10)-H''(C10)	114 (1)
H'(C10)-C(10)-C(8)	109 (1)
H'(C10)-C(10)-H''(C10)	109 (2)
H''(C10)-C(10)-C(8)	105 (1)

Fig. 3. Hydrogen-bonded system in the structure of *dl*-carvoxime. Distances are in Å, angles in degrees.

model calculations (Del Bene, 1972): $r_{O...N} = 2·78$ Å, $N-H···O = 154°$. No other molecular contacts of particular interest are present.

Our thanks are due to Drs A. J. M. Duisenberg and G. Roelofsen for assistance.

References

ADRIANI, J. H. (1900). *Z. phys. Chem.* **33**, 453–476.

BAERT, F. & FOURET, R. (1975). *Cryst. Struct. Commun.* **4**, 307–310.

BEYER, P. (1891). *Z. Kristallogr.* **18**, 296–298.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DEL BENE, J. E. (1972). *J. Chem. Phys.* **57**, 1899–1908.

JACQUES, J. (1970). Personal communication.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN, A Computer Program for the Automatic Solution of Crystal Structures*, Univ. of York Printing Unit, York.

OONK, H. A. J. (1965). Thesis, Univ. of Utrecht.

ROOZEBOOM, H. W. B. (1891). *Z. phys. Chem.* **8**, 504–535.

ROOZEBOOM, H. W. B. (1899). *Z. phys. Chem.* **28**, 494–517.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). X-RAY System, Univ. of Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAMMANN, G. (1914). *Z. phys. Chem.* **87**, 357–365.

VAN LAAR, J. J. (1908). *Z. phys. Chem.* **64**, 289–291.