

Plan C(6), C(8a), C(7), C(8)

$$-0,55848x - 0,35838y + 1,07592z = 4,49906$$

[C(6) 0,005 Å; C(8a) -0,004 Å; C(7) -0,011 Å;
C(8) 0,010 Å.]

Plan C(3a), C(4), C(5)

$$+1,31348x + 0,39949y - 1,03100z = -2,37055$$

Les angles entre ces plans, comme le montre la Fig. 3, sont de 48 et de 27°, valeurs identiques aux erreurs près, à celles trouvées dans l'acide thujiq.ue.

Le cycle tropilidénique du composé étudié présente donc une conformation bateau avec les caractéristiques suivantes:

- un carbone tétraédrique C(4),
- un système de simples et doubles liaisons alternées,
- deux angles entre plans caractéristiques de 48 et 27°.

Dans le ligand libre, les carbones C(3a) et C(8a) sont de type sp^2 . Les carbones C(4) et C(8) sont donc toujours situés dans le plan thiophénique. Etant donné le type sp^3 de l'atome de carbone C(4), les atomes de carbone C(5), C(6), C(7) sont rejetés en dehors du plan moyen thiophénique. Pour interpréter l'unicité de la raie de résonance des protons méthyléniques (déplacement chimique moyen $\delta = 3,14$ p.p.m.), il faut admettre l'existence d'une résonance entre les deux conformations possibles du cycle tropilidénique plaçant alternativement les atomes C(5), C(6), C(7) de part et d'autre du plan thiophénique. Les protons géminés du carbone tétraédrique occupent alors statistiquement une position axiale ou équatoriale.

Dans le ligand complexé, l'examen des distances des atomes au plan moyen défini par les quatre carbones du cycle thiophénique montre que les atomes de carbone C(4) et C(8) s'écartent très légèrement de ce plan

(0,08 et 0,02 Å). Ceci montre que les atomes de carbone C(3a) et C(8a) comme les atomes C(3) et C(1) ont perdu une partie de leur caractère sp^2 par suite de la présence du coordinat $Cr(CO)_3$. Comme dans le ligand libre, les atomes C(5), C(6) et C(7) sont rejetés en dehors du plan moyen thiophénique. Mais la présence du coordinat $Cr(CO)_3$ détermine un marquage latéral de la molécule. Les deux conformations bateau du cycle tropilidénique ne sont plus énergétiquement équivalentes; seule la conformation bateau plaçant les atomes C(5), C(6), C(7) et le trépied de part et d'autre du plan moyen thiophénique est possible; l'autre conformation est exclue par empêchement stérique. Les protons méthyléniques ne sont donc plus magnétiquement équivalents, et apparaissent sous la forme d'un doublet dans le spectre r.m.n.

Les résultats cristallographiques confirment de façon indiscutable les données obtenus en r.m.n. De plus, ils apportent des renseignements sur l'influence de la complexation sur un noyau hétérocyclique: diminution du caractère de simples et doubles liaisons C-C, allongement des liaisons S-C(1) et S-C(3) et absence de planéité du cycle.

Références

- DAVIS, R. E. & TULINSKY, A. (1966). *J. Amer. Chem. Soc.* **88**, 4583-4588.
- DOERING, W. VON E. & KNOX, L. M. (1954). *J. Amer. Chem. Soc.* **76**, 3203-3206.
- DUSAUSOY, Y. (1972). Thèse. Université de Nancy I, No. d'ordre AO 6729.
- GUILARD, R., TIROUFLET, J. & FOURNARI, P. (1971). *J. Organometal.* **33**, 195-213.
- International Tables of X-ray Crystallography* (1969). Vol. I. Birmingham: Kynoch Press.
- SCHOMAKER, V. & PAULING, L. (1939). *J. Amer. Chem. Soc.* **61**, 2643.
- TRAETTEBERG, M. (1964). *J. Amer. Chem. Soc.* **86**, 458-462.

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The Crystal Structure of DL-Isoleucine and Structural Relations between Racemic and Optically Active Pairs in some Aminoacids

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DL-Isoleucine belongs to the space group $P\bar{1}$, with $a = 14.66$, $b = 5.39$, $c = 5.27$ Å, $\alpha = 109.2^\circ$, $\beta = 114.0^\circ$ and $\gamma = 85.2^\circ$. The structure has been determined with moderate accuracy, and shows some relationships with the L and DL forms of other amino acids.

It has recently been shown (Torii & Itaka, 1971) that the crystal structure of some L- α -amino acids having hydrocarbon side chains are closely related. On the other hand, it has been pointed out (Pedone & Benedetti, 1971) that an equally close relationship may occur, in some cases, between the molecular packings

of racemic and optically active pairs. Such a relationship can be practically utilized to obtain a very good approximation to the crystal structure of either the racemic or optically active form, from that of the other. In this communication we report the crystal structure of DL-isoleucine and show that the same simple re-

Table 1. Crystal parameters of the L- and DL-forms of some amino acids

Compound	Molecules per unit cell						References
	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	
L-Valine	9.71 (1)	5.27 (2)	12.06 (2)	—	90.8 (2)	—	Torii & Iitaka (1970)
DL-Valine	5.21 (2)	22.10 (4)	5.41 (2)	—	109.2	—	Maillikarijunnan & Thyagaraja Rao (1969)
L-Isoleucine	9.75 (2)	5.32 (2)	14.12 (2)	—	95.8 (2)	—	Torii & Iitaka (1971)
DL-Isoleucine	14.66 (4)	5.39 (2)	5.27 (2)	—	114.0 (3)	85.2 (3)	This paper
L-Tyrosine	6.913 (5)	21.116 (3)	5.829 (4)	—	—	—	Mostad <i>et al.</i> (1973)
DL-Tyrosine	20.836 (8)	6.810 (2)	5.905 (2)	—	—	—	Mostad & Rømming (1973)

lations exists between the molecular packing of DL- and L-isoleucine, and DL- and L-valine.*

A sample of 'DL-isoleucine' from the Nutritional Biochemical Corporation was used from which rather poor crystals were obtained by crystallization from water.

The X-ray analysis showed that the crystals were, in fact, solid solutions of the two diastereoisomeric pairs, corresponding to the two asymmetric centres of the molecule, in a ratio not significantly different from 1:1. The X-ray diffraction data were collected on an automated four-circle Siemens diffractometer. The determination of the lattice constants (see Table 1) was carried out by a least-squares treatment of 2θ , χ , φ ,

* This relationship is also verified for the DL- and L-tyrosine (Mostad, Nissen & Rømming, 1971; Mostad & Rømming, 1972), and very likely for L- and DL-cysteine, although the structure of the latter is not known (Harding & Long, 1968).

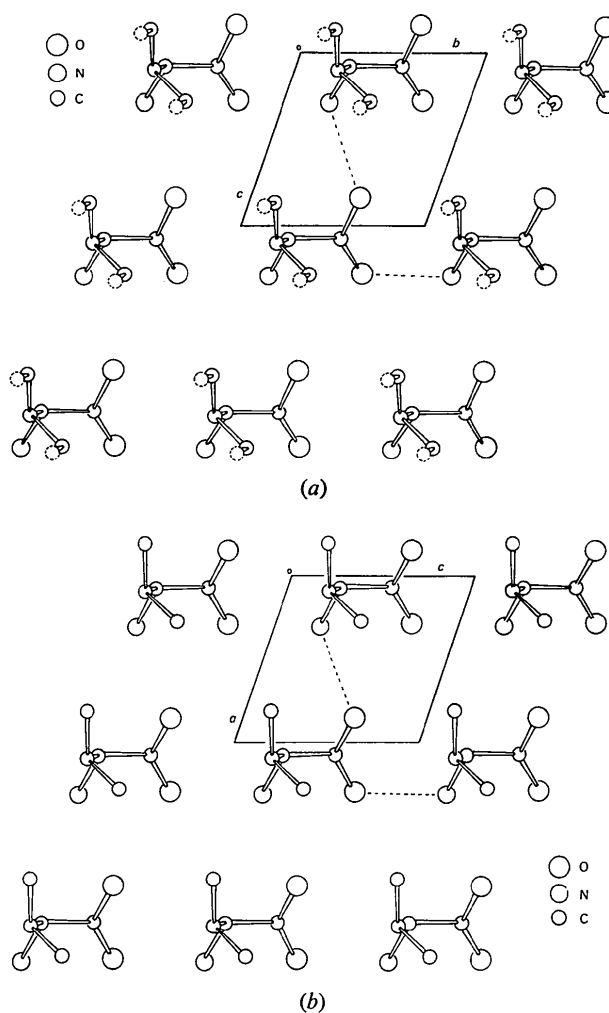


Fig. 1. (a) Projection perpendicular to the *bc* plane of a layer of iso-configurational (L) molecules of DL-isoleucine. (b) Projection perpendicular to the *ac* plane of a layer of iso-configurational (L) molecule of DL-valine.

setting angles for 22 reflexions with $2\theta > 80^\circ$. (Cu $K\alpha$ $\lambda = 1.5418 \text{ \AA}$). 955 non-zero independent reflexions were measured, using a θ - 2θ scan-mode. All the crystals examined were twinned, the two lattices having the $hk0$ planes in common.

The crystal structure was solved on the basis of some evident relationships (see Table 1):

(i) The lattice dimensions of the ac plane of DL-valine are almost identical with the dimensions of the bc plane of DL-isoleucine.

(ii) The length of the c axis and the intensity of the $00l$ reflexions of L-isoleucine were very similar to the a axis and $h00$ intensities of DL-isoleucine.

A molecular model of L-isoleucine was packed in the

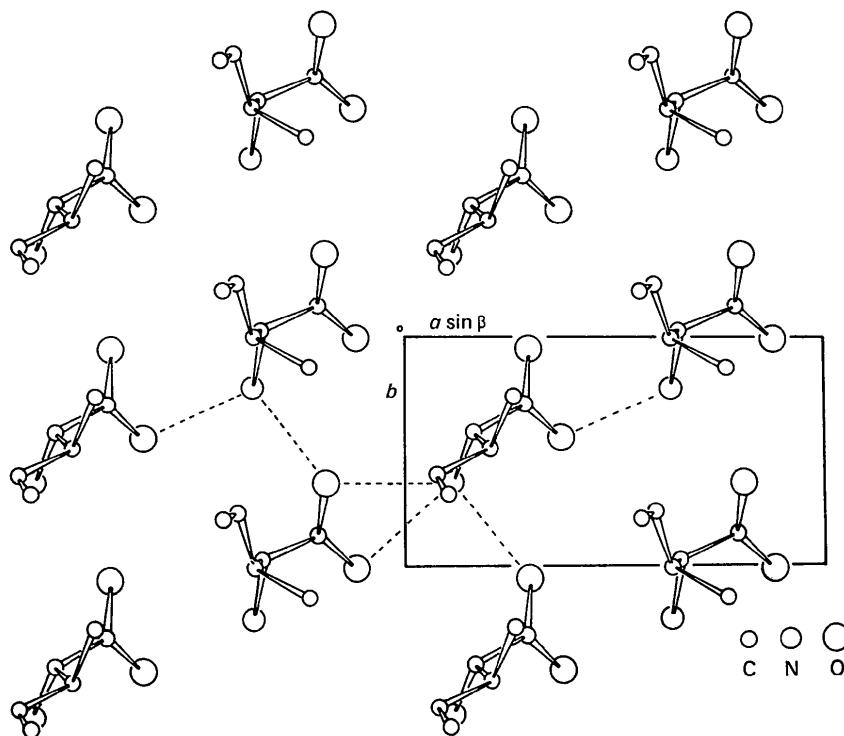


Fig. 2. Projection along the c axis of a layer of molecules of L-isoleucine.

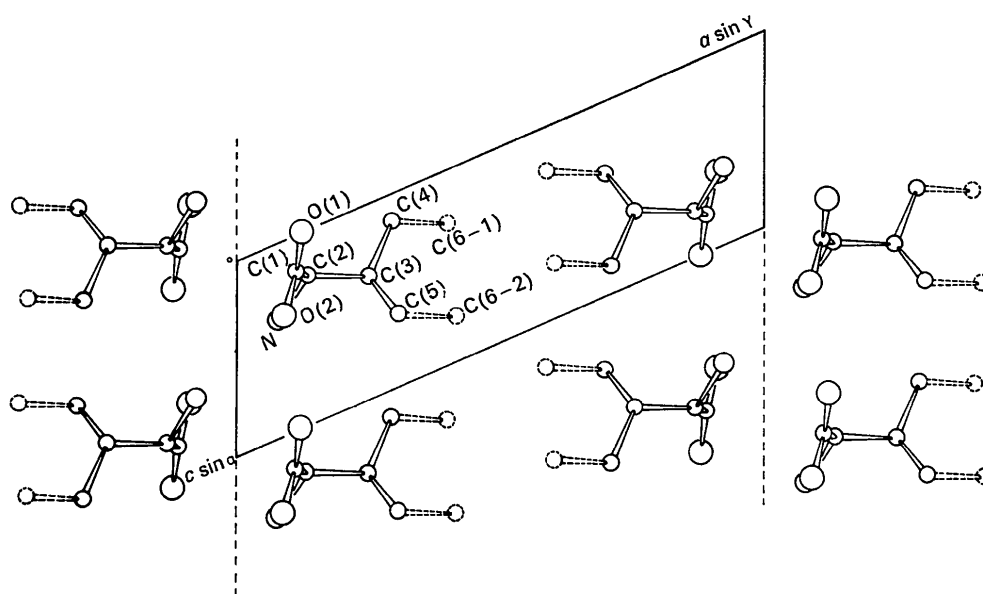


Fig. 3. Projection along the b axis of the crystal structure of DL-isoleucine.

bc plane of DL isoleucine in the same way as found in the *ac* plane of DL-valine. The *R* factor for this first trial model was 0.24. A difference Fourier synthesis soon indicated the presence in the same site of two diastereoisomeric molecules.

The structure was refined by least-squares methods with anisotropic thermal parameters for all atoms except those [C(4), C(5), C(6-1), C(6-2)] involved in the statistical substitution. No attempt was made to locate the hydrogen atoms. The final conventional *R* value is 0.15, which should be considered an acceptable value on the basis of the poor quality and twinning of the crystals, and the partially statistical nature of the structure.

The structural feature common to the four crystals is the presence of layers containing hydrogen bonded molecules having the same configuration (in the particular case of our sample of DL-isoleucine, we refer to the configuration of the α -carbon atom only). The relationship between such layers in DL-isoleucine and DL-valine is of quasi-identity [Fig. 1(a) and (b)]. This is an indication of the predominant role played by the hydrogen bonding compared with the side-chain interactions. Significant, but still small, differences distinguish the packing of iso-configurational molecules in DL and L crystals [Fig. 2, *cf.* Fig. (a) and (b)].

A second crystallographically independent molecule appears in the L crystals with a different conformation on the side chain. In both racemic and optically active

forms, molecular layers are tightly associated in pairs *via* hydrogen bonding. The coupled layers are crystallographically related by inversion centres in the racemic forms and by binary screw axes in the optically active ones.

The crystals are built up by a sequence of such pairs of molecular layers related by an unitary lattice translation (Fig. 3) or, as in DL-valine, by a 2_1 symmetry operation.

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References

- HARDING, M. M. & LONG, H. A. (1968). *Acta Cryst.* B24, 1096–1102.
 MALLIKARJUNAN, M. & THYAGARAJA RAO, S. (1969). *Acta Cryst.* B25, 296–303.
 MOSTAD, A., NISSEN, H. M. & RØMMING, C. (1973). *Acta Chem. Scand.* In the press.
 MOSTAD, A. & RØMMING, C. (1973). *Acta Chem. Scand.* In the press.
 PEDONE, C. & BENEDETTI, E. (1972). *Acta Cryst.* B28, 1970–71.
 TORII, K. & IITAKA, Y. (1970). *Acta Cryst.* B26, 1317–1326.
 TORII, K. & IITAKA, Y. (1971). *Acta Cryst.* B27, 2237–2246.

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The Crystal Structure of (+)₅₈₉-*cis*- β -Dinitro-(*R*-5-methyltriethylenetetramine)cobalt(III) Chloride, (+)₅₈₉-*cis*- β -[Co(NO₂)₂(*R*-5-metrien)]Cl

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The structure of (+)₅₈₉-*cis*- β -[Co(NO₂)₂(*R*-5-metrien)]Cl has been determined from three-dimensional X-ray data collected by diffractometer. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions: $a = 12.696$, $b = 14.364$ and $c = 7.542$ Å. There are four formula units in the unit cell. The structure was solved by the heavy-atom method and refined by the anisotropic block-diagonal least-squares method to an *R* value of 0.069 for 1567 observed reflexions. The quadridentate ligand is linked to the central cobalt atom with its four nitrogen atoms in *cis*- β coordination. A substituted methyl group lies in an equatorial position relative to the plane of the chelate ring. It is attached to the carbon atom next to the secondary nitrogen atom common to the two chelate rings both in the equatorial plane of the octahedron. The absolute configuration of the complex ion can be described as a skew chelate pair, *A*. The conformation of the chelate ring with the methyl group is λ and those of the other two are δ and λ , respectively. The absolute configurations of the two secondary nitrogen atoms are both *S*.

Introduction

This study of (+)₅₈₉-*cis*- β -dinitro(*R*-5-methyltriethylenetetramine)cobalt(III) chloride,

(+)₅₈₉-*cis*- β -[Co(NO₂)₂(*R*-5-metrien)]Cl,
R-5-metrien:

H₂NCH₂CH₂NHCH(CH₃)CH₂NHCH₂CH₂NH₂,
 is part of the crystal structure analysis of substituted triethylenetetraminecobalt(III) complexes (Ito, Marumo & Saito, 1970, 1972*a*, *b*). The authors were interested in comparing the geometries of trien ligands.