benzene (Farag, 1954) the rings are twisted by ~30° and in hexamethylbenzene (Bart, 1968) the phenyl groups are twisted *ca* 65° from the plane of the central ring. In the low-temperature form of *p*-terphenyl (Baudour, Delugeard & Cailleau, 1976) there is a double minimum in the potential well so that the twist angle can be near 16 or 25°. In the related compounds 1,8-diphenylnaphthalene, *peri*-diphenylacenaphthene and in 1,4,5,8-tetraphenylnaphthalene the torsion angles are found to be 67, 57 and 58° respectively. The large variation in this parameter stresses the dependence on molecular environment.

After this work was complete our attention was drawn to another determination of the structure of the title compound (Korp, 1975). The essential features of the structure are consistent in the two determinations.

References

BART, J. C. J. (1968). *Acta Cryst.* B24, 1277–1287.

BAUDOUR, J. L., DELUGEARD, Y. & CAILLEAU, H. (1976). *Acta Cryst.* B32, 150–154.

CHARBONNEAU, G. P. & DELUGEARD, Y. (1976). *Acta Cryst.* B32, 1420–1423.

CHARBONNEAU, G. P. & DELUGEARD, Y. (1977). *Acta Cryst.* B33, 1586–1588.

DEWAR, M. J. S. & HARGET, A. J. (1970). *Proc. R. Soc. London Ser. A*, 315, 443–464.

FARAG, M. S. (1954). *Acta Cryst.* 7, 117–121.

GAVEZZOTTI, A. & SIMONETTA, M. (1975). *Acta Cryst.* A31, 645–654.

GAVEZZOTTI, A. & SIMONETTA, M. (1976). *Acta Cryst.* A32, 997–1001.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* 3, 210–214.

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

JONES, W. (1976). *Surface and Defect Properties of Solids*, edited by M. W. ROBERTS & J. M. THOMAS. *Chem. Soc. Spec. Publ.* 5, 65–80.

JONES, W., RAMDAS, S. & THOMAS, J. M. (1978). *Chem. Phys. Lett.* In the press.

KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules.* New York: Academic Press.

KITAIGORODSKY, A. I. & MIRSKAYA, K. V. (1972). *Mater. Res. Bull.* 7, 1271–1280.

KORP, J. D. (1975). PhD Thesis, Univ. of Texas at Austin, Texas.

MASON, R. (1964). *Acta Cryst.* 17, 547–555.

PARKINSON, G. M. (1978). PhD Thesis, Univ. of Wales, Aberystwyth.

RAMDAS, S. & THOMAS, J. M. (1976). *J. Chem. Soc. Faraday Trans.* 2, 72, 1251–1258.

RAMDAS, S., THOMAS, J. M. & GORINGE, M. J. (1977). *J. Chem. Soc. Faraday Trans.* 2, 73, 551–561.

RIETVELD, H. M., MASLEN, E. N. & CLEWS, C. J. B. (1970). *Acta Cryst.* B26, 693–706.

ROBERTSON, G. B. (1961). *Nature (London)*, 191, 593–594.

SLOAN, G. (1975). Personal communication to J. M. THOMAS.

TROTTER, J. (1961). *Acta Cryst.* 14, 1135–1140.

WILLIAMS, D. E. (1969). *Acta Cryst.* A25, 464–470.

WILLIAMS, D. E. (1972). *Acta Cryst.* A28, 629–635.

WILLIAMS, D. E. (1974). *Acta Cryst.* A30, 71–77.

Static Disorder in a True Racemate: 3-(*o*-Chlorophenylimino)camphor

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Abstract

The phase diagram between the (+) and (±) forms of the title compound, $C_{16}H_{18}ClNO$, suggests that this system should give solid solutions at all compositions. The structures of the two forms were solved at room temperature. The (±) form is monoclinic, space group $P2_1/a$, with $Z = 4$, $a = 13.795$ (28), $b = 10.442$ (21), $c = 10.464$ (21) Å, $\beta = 105.08$ (3). The (±) form is a true but disordered racemate. The computation of the intramolecular energy proves the possible existence of three different molecular conformations found in the structure of (+) and (±) forms. R was 7.5% $[I \geq 3\sigma(I)]$ and 5.8% $[I \geq 4\sigma(I)]$ for the (+) and (±) forms respectively.

Introduction

This work is part of a general study of solid solutions between antipodes. The phase diagram (Fig. 1) (Jacques & Leclerc, 1972) exhibits a minimum for the racemic composition [m.p. of the (+) antipode is 397–399 K, m.p. of the (±) form is 380 K] and is known as type III (Roozeboom, 1899). According to this piece of information it should be possible to obtain mixed crystals of the two enantiomorphs at all compositions of the (+) and (−) forms. The crystal structures of the (+) and (±) forms were determined in order to elucidate the problem of the syncrystallization of the two antipodes.

The structural study of the active form has been published (Baert, Foulon & Fouret, 1975).

Experimental

(a) Preparation

The (±) compound was synthesized by Dvolaitzky (1969) according to a method described by Singh &

Seth (1956). The crystals, obtained by evaporation from methanol, are yellow, transparent parallelepipeds elongated along c. The density was measured by flotation.

(b) Unit cells, space groups

The crystallographic data are reported in Table 1.

(c) Intensity data

Intensities for 2070 reflections [1412 with $I \geq 4\sigma(I)$] were measured at room temperature by the ω–2θ scan on a Philips four-circle diffractometer. The data were corrected for Lorentz and polarization factors, but not for absorption or extinction. An absolute scale factor and the mean isotropic temperature coefficient were obtained by Wilson's (1942) method. The distribution of normalized structure factors suggested a centrosymmetric structure.

Structure determination and refinement

The structure was solved with MULTAN (Germain & Woolfson, 1968). The structure of the (±) form was first determined from Weissenberg photographs. A Fourier map permitted location of the non-hydrogen atoms except C(4) (for numbering see Fig. 2) which was put at its expected position. Full-matrix least-squares refinement led to anomalies in the intramolecular distances and temperature factors of the atoms belonging to the camphor group [C(4)–C(5) = 1·73, C(1)–C(6) = 1·76, C(5)–C(6) = 1·38 Å]. On a difference map, ten H atoms could be located, but a puzzling high residual electron density (0·9 e Å^{-3}) appeared in the vicinity of C(1) and C(4)–C(9). R was then 10·6% for 1100 reflections.

Table 1. Crystallographica data

$C_{16}H_{18}ClNO$
FW = 275·78
$\lambda(Cu\ K\alpha) = 1·5418$ Å
$\mu(Cu\ K\alpha) = 1·95$ mm^{-1}
$F(000)$ = 584

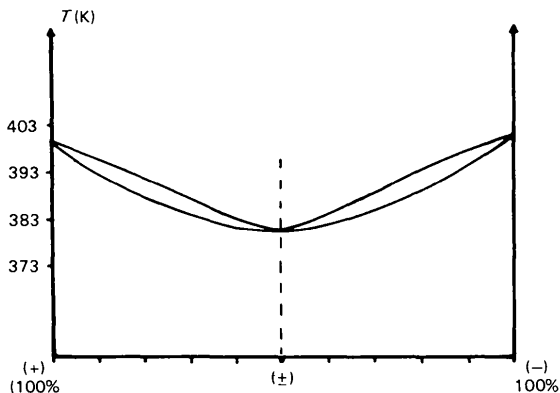| (+) Form Orthorhombic $P2_12_12_1$	(±) Form Monoclinic $P2_1/a$
a = 16·475 (33) Å	a = 13·795 (28) Å
b = 12·323 (24)	b = 10·442 (21)
c = 7·391 (14)	c = 10·464 (21)
V = 1500 Å^3	β = 105°08'
Z = 4	V = 1455 Å^3
D_x = 1·22 Mg m^{-3}	Z = 4
D_m = 1·23	D_x = 1·26 Mg m^{-3}
	D_m = 1·23

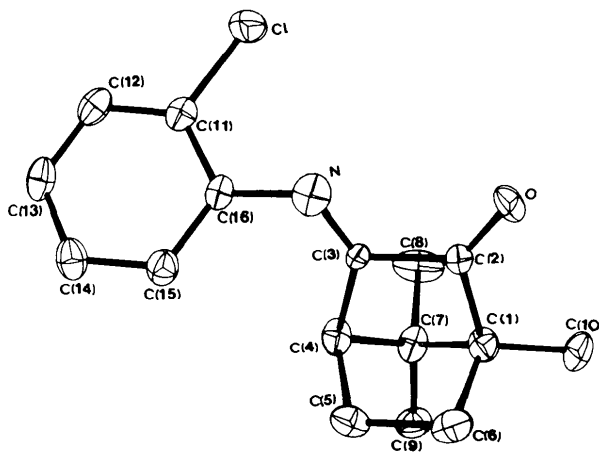Fig. 1. Solid–liquid equilibrium diagram of mixtures of (+)- and (−)-3-(o-chlorophenylimino)camphor.

Fig. 2. Perspective drawing of the molecule (occupancy factor 0·72) to show the numbering of atoms.

To be sure of our data 2070 intensities were measured on a four-circle diffractometer.

The procedure of refinement is described by Baert, Fouret, Oonk & Kroon (1978). At first the camphor group found in the ($\pm$) crystal was adjusted on the known structure in the (+) antipode (assuming that the conformations are nearly the same). The structure was then refined by rigid-body least-squares calculations with *ORION* (André, Fourme & Renaud, 1971), which allows the refinement of rigid groups of atoms by translation and rotation. *R* was 13·4% for 1050 structure factors.

A difference synthesis always showed residual electronic density (1·2 e Å^{-3}), but the highest peaks could be interpreted as a disordered camphor group (Fig. 3) occupying the same site as found in the molecule previously.

After adjusting this new molecule, the refinement converged to $R = 5\cdot8\%$ for the 1412 structure factors $[I \geq 4\sigma(I)]$, without anomalies. The occupancy factors (0·72, 0·28) were obtained by least-squares refinement. Fig. 4 shows the relative positions of the two molecules. The intramolecular distances between C(4), C(5), C(6), C(1) remain correct after a refinement of the atomic parameters of C(5) and C(6). The remaining H atoms are placed geometrically for the two molecules.

Scattering factors are those of Hanson, Herman, Lea & Skillman (1964). The final parameters are listed in Table 2.*

Results and discussions

(a) Intramolecular results

Bond lengths and angles are reported in Table 3 and are normal.

(b) Comparison between the different conformations found in the (+) and ($\pm$) crystals

Three different conformations of the molecule were found and denoted $C(+)$ [in the (+) crystal], A (0·72) and B (0·28) [in the ($\pm$) crystal]. Fig. 5 is a schematic
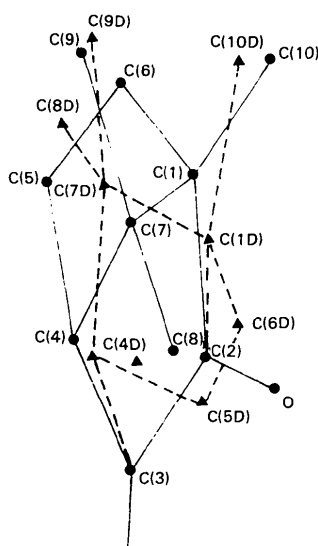

Fig. 3. The disorder. Atoms marked *D* belong to the disordered camphor group.
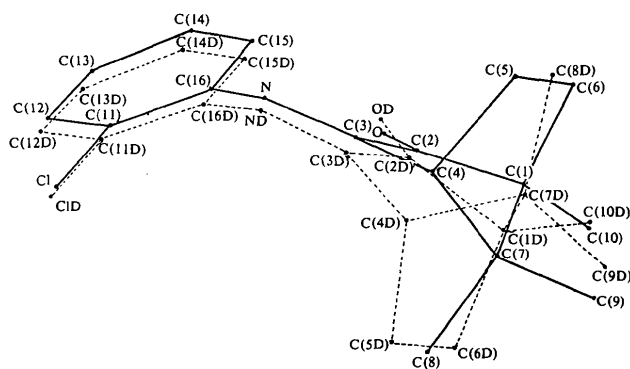
Fig. 4. Relative positions of molecules *A* and *B* (atoms marked *D*) occupying the same site.
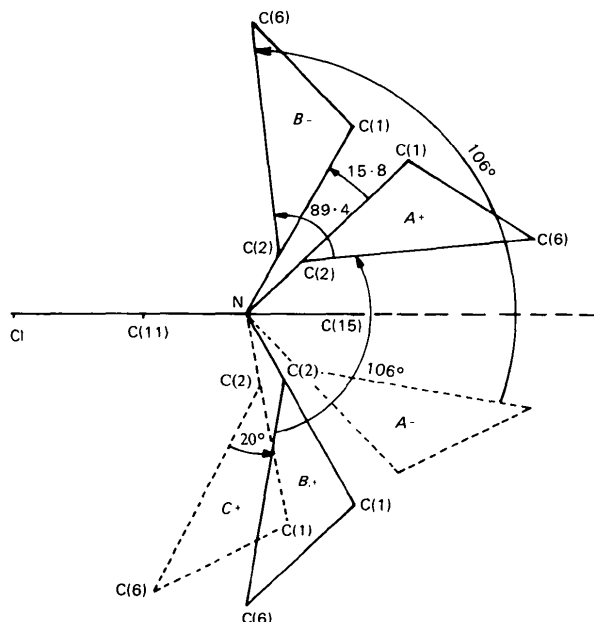

Fig. 5. Schematic projection of the different conformations.

projection parallel to C(16)—N of these three conformations. (The benzene ring is perpendicular to the plane of the figure and the camphor group looks like a triangle.) The three right (left) molecules are obtained by rotation of the camphor group about C(16)—N (C_+ to $B_+ = 20°$, B_+ to $A_+ = 106°$). A computation of the intramolecular energy (atom–atom potentials) of the molecule around C(16)—N (Fig. 6) shows that the A, B, C conformations have nearly the same energy and confirms their possible existence in the crystal.

(c) Molecular packing

The unit cell always contains an equal number (two) of the two antipodes. The same crystallographic site can be occupied by two antipodes with conformations

A or B [A_+ (0·72), B_- (0·28) or A_- (0·72), B_+ (0·28)]. Fig. 7 is a projection along b of the cell contents (upper part A molecules, lower part B molecules).

The ($\pm$) crystal is a disordered true racemate with a non-statistical $\bar{1}$ symmetry element.

The k packing coefficient (Kitaigorodskii, 1973) is 0·73, which suggests a relatively compact structure. The shortest intermolecular distances between Cl, N, O, C atoms are shown in Fig. 8. The H—H distances are generally shorter than in the (+) crystal in agreement with the fact that the cell volume is lower in the ($\pm$) than in the (+) form. The molecules are bound by van der Waals contacts only.

The structure can be described by two chains parallel to the direction [100]; the camphor groups of one of them faces the chlorophenyl groups of the other. This particular packing was also observed in the active form.

Table 2. *Atomic parameters* (*atoms marked D belong to molecule B, occupancy factor* 0·28)

(a) Heavy atoms, fractional positional parameters ($\times 10^4$)
(No e.s.d.'s are given because of the rigid-body refinement.)

	x	y	z
Cl	4152	1815	7220
C(11)	5316	2476	7957
C(12)	6168	1745	8066
C(13)	7097	2292	8628
C(14)	7165	3525	9098
C(15)	6293	4262	8980
C(16)	5354	3751	8388
N	4447	4413	8281
O	2571	5872	7813
C(1)	3539	7572	7165
C(2)	3331	6259	7619
C(3)	4318	5534	7782
C(4)	4983	6469	7333
C(5)	5288	7476	8491
C(6)	4314	8194	8380
C(7)	4239	7225	6289
C(8)	3705	6343	5120
C(9)	4697	8393	5749
C(10)	2615	8357	6625
ClD	4028	1727	7112
ND	4371	4337	8125
OD	2602	5813	7973
C(1)D	3365	7310	6586
C(2)D	3270	6172	7500
C(3)D	4240	5389	7586
C(4)D	4811	6113	6735
C(5)D	4182	5901	5257
C(6)D	3191	6674	5164
C(7)D	4548	7522	7034
C(8)D	2658	8457	6653
C(9)D	4916	8525	6138
C(10)D	4945	7917	8493
C(11)D	5206	2367	7812
C(12)D	6044	1611	7918
C(13)D	6984	2140	8451
C(14)D	7077	3383	8896
C(15)D	6218	4145	8781
C(16)D	5269	3652	8218

(b) Hydrogen atoms, fractional positional parameters ($\times 10^3$)
(molecule A occupancy factor 0·72)

	x	y	z	B (Å²)
HC(4)	564	596	721	4·0
HC(5)	554	702	946	6·0
H'C(5)	586	815	838	6·0
HC(6)	404	805	906	5·4
H'C(6)	439	921	823	5·4
HC(8)	241	865	741	5·5
H'C(8)	212	777	595	5·5
H''C(8)	283	903	613	5·5
HC(9)	520	899	665	4·8
H'C(9)	409	860	526	4·8
H''C(9)	516	813	528	4·8
HC(10)	426	594	466	4·0
H'C(10)	331	556	545	4·0
H''C(10)	318	690	440	4·0
HC(12)	611	77	76	3·8
HC(13)	778	173	872	4·4
HC(14)	790	393	956	3·9
HC(15)	635	524	934	3·4

(c) Hydrogen atoms, expected positional parameters ($\times 10^3$)
(molecule B occupancy factor 0·28)

	x	y	z	B (Å²)
HC(4)D	556	573	691	5·0
HC(5)D	400	490	505	5·0
H'C(5)D	455	627	454	5·0
HC(6)D	254	606	498	5·0
H'C(6)D	307	741	443	5·0
HC(8)D	204	800	618	5·0
H'C(8)D	274	866	768	5·0
H''C(8)D	279	926	626	5·0
HC(9)D	430	776	566	5·0
H'C(9)D	485	937	609	5·0
H''C(9)D	550	821	596	5·0
HC(10)D	571	805	843	5·0
H'C(10)D	495	736	936	5·0
H''C(10)D	461	884	859	5·0
HC(12)D	598	063	760	3·8
HC(13)D	766	156	854	4·4
HC(14)D	782	378	933	3·9
HC(15)D	629	513	912	3·4

Table 3. *Bond lengths* (Å) *and angles* (°) *for molecule
A* (*occupancy factor* 0·72)

(E.s.d.'s are not given because of the type of refinement.)

Cl–C(11)	1·733	C(11)–C(12)	1·380	C(12)–C(13)	1·386
C(13)–C(14)	1·373	C(14)–C(15)	1·373	C(14)–C(15)	1·406
C(15)–C(16)	1·388	C(16)–C(11)	1·373	C(16)–N	1·408
N–C(3)	1·275	C(3)–C(2)	1·528	C(2)–C(1)	1·503
C(2)–O	1·188	C(1)–C(6)	1·573	C(1)–C(10)	1·497
C(1)–C(7)	1·538	C(6)–C(5)	1·517	C(5)–C(4)	1·577
C(4)–C(3)	1·497	C(4)–C(7)	1·512	C(7)–C(8)	1·555
C(7)–C(9)	1·546				

C1–C(11)–C(16)	118·3	Cl–C(11)–C(12)	119·1
C(11)–C(12)–C(13)	118·8	C(12)–C(13)–C(14)	120·5
C(13)–C(14)–C(15)	120·3	C(14)–C(15)–C(16)	120·4
C(15)–C(16)–C(11)	117·5	C(16)–C(11)–C(12)	122·5
C(11)–C(16)–N	118·8	C(15)–C(16)–N	123·6
C(16)–N–C(3)	120·6	N–C(3)–C(2)	121·7
N–C(3)–C(4)	134·1	C(2)–C(3)–C(4)	104·1
C(3)–C(2)–O	127·7	C(3)–C(2)–C(1)	104·4
C(2)–C(1)–C(10)	113·9	C(6)–C(1)–C(10)	114·3
C(2)–C(1)–C(6)	105·5	C(2)–C(1)–C(7)	100·1
C(6)–C(1)–C(7)	100·3	C(1)–C(6)–C(5)	105·1
C(6)–C(5)–C(4)	102·5	C(5)–C(4)–C(3)	104·9
C(5)–C(4)–C(7)	101·7	C(1)–C(7)–C(4)	96·1
C(3)–C(4)–C(7)	101·7	C(1)–C(7)–C(9)	114·3
C(1)–C(7)–C(8)	111·4	C(4)–C(7)–C(8)	110·7
C(4)–C(7)–C(9)	114·2	C(8)–C(7)–C(9)	109·6
C(1)–C(2)–O	127·8		

Fig. 7. Projection along *b* of the cell contents (upper part *A*
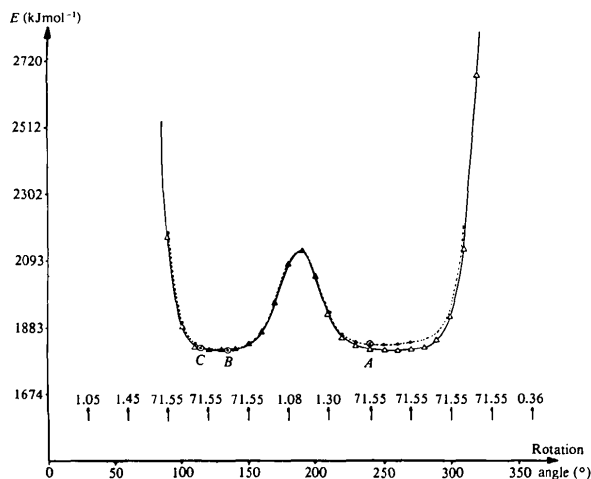molecules, lower part *B* molecules).

Fig. 6. Energy of conformation *versus* angle of rotation about
C(16)–N. ⊗ *C*, molecule in the (+) crystal; ⊗ *A*, molecule in the
(±) crystal (occupancy factor 0·72); ⊗ *B*, molecule in the (±)
crystal (occupancy factor 0·28). For any important angles, the
shortest distance between two atoms is reported.

Fig. 8. Shortest distances between atoms of molecule *A* in
projection along *b*.

Table 1 shows the differences between the (+) and the
(±) crystal. The results often contradict the Kitai-
gorodskii (1973) laws about the conditions for the
formation of mixed crystals (similarity of shape of the
molecules, equal packing, same crystallographic system,
etc.).

In fact, in this case, despite the phase diagram, a
mixture of 50% (±) and 50% (+) compounds gave no
mixed crystals but the racemate. We could not obtain
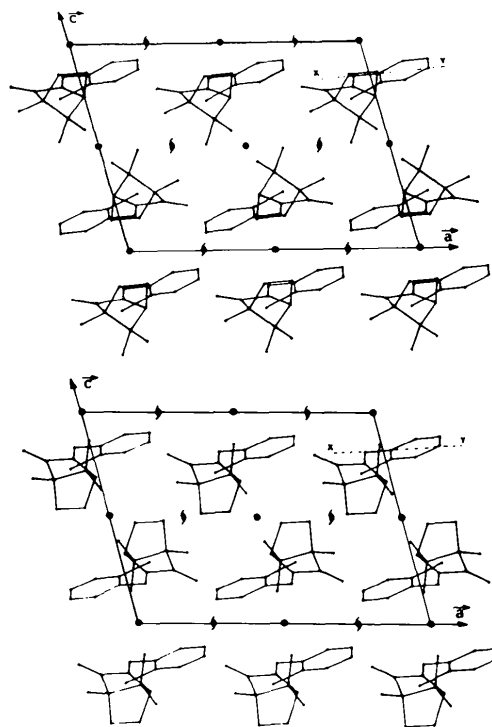solid solutions at room temperature with this system. A

study of the racemate on a polarizing microscope with
a heating stage revealed a crystal–crystal trans-
formation at a temperature near the melting point. This
certainly prohibits the possibility of obtaining solid
solutions at high temperature.

References

ANDRÉ, D., FOURME, R. & RENAUD, M. (1971). *Acta Cryst.* B27, 2371–2380.

BAERT, F., FOULON, M. & FOURET, R. (1975). *Cryst. Struct. Commun.* 4, 61–66.

BAERT, F., FOURET, R., OONK, H. A. J. & KROON, J. (1978). *Acta Cryst.* B34, 222–226.

DVOLAITZKY, M. (1969). *C. R. Acad. Sci.* 268, 1811–1813.

GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* B24, 91–96.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1044.

JACQUES, J. & LECLERC, M. (1972). Private communication.

KITAIGORODSKII, A. I. (1973). *Molecular Crystals and Molecules.* New York: Academic Press.

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

SINGH, B. K. & SETH, S. K. (1956). *J. Indian Chem. Soc.* 33, 491–502.

WILSON, A. J. C. (1942). *Nature* (*London*), 150, 151–152.

The Crystal Structure of Imidazole at 103 K by Neutron Diffraction

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Abstract

At 103 K, imidazole, $C_3H_4N_2$, is monoclinic, space group $P2_1/c$, with four molecules per unit cell and has lattice parameters $a = 7.569$ (1), $b = 5.366$ (1), $c = 9.785$ (2) Å, and $\beta = 119.08$ (1)°. The neutron structure determination using 1095 reflections gave $R(F^2) = 0.026$ and $R_w(F^2) = 0.041$. The e.s.d.'s in bond lengths (0.001 Å for C—C, C—N) and angles are smaller than in previous X-ray and neutron determinations of this structure. The improved precision was needed in connection with an X-ray study of the charge density of imidazole.

Introduction

Neutron structure determinations of imidazole (Fig. 1) at 293 K and 123 K have been reported by Craven, McMullan, Bell & Freeman (1977), hereafter CMBF. In a subsequent low-temperature X-ray determination by Epstein, Ruble & Craven (1978), hereafter ERC, the crystal was cooled in a stream of nitrogen gas at a recorded temperature of 123 K. However, it was noted (Table 1) that there were significant differences in the

X-ray cell parameters from the 123 K values of Martinez-Carrera (1966). Also, in least-squares refinements of the structure using reflections with sin $\theta/\lambda > 1.0$ Å^{-1}, the carbon and nitrogen X-ray U_{ij} values were found to be substantially different from the corresponding CMBF neutron values. These differences
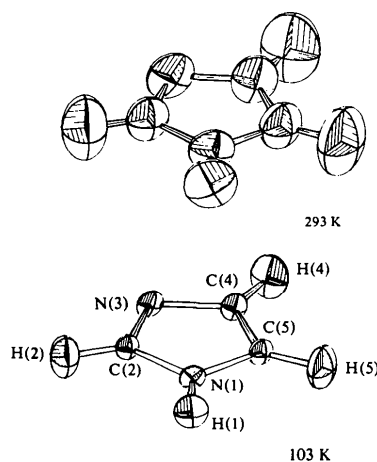

Fig. 1. Atomic nomenclature for imidazole and 50% probability ellipsoids (Johnson, 1976).