Acta Cryst. (1999). B**55**, 375–379

Thermal vibrations in potassium 3-benzoyl-2-thiophenecarboxylate

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(*Received 14 May 1998; accepted 5 October 1998*)

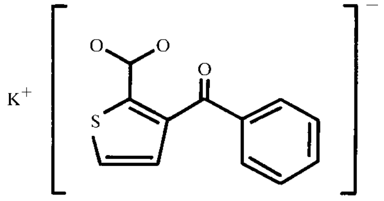
This work is dedicated in memory of Professor Kenneth N. Trueblood

Abstract

The atomic thermal displacement parameters at 293 K for the anion in the title salt have been analyzed in terms of a body having two rigid segments, namely the benzoyl and the 2-thiophenecarboxylate groups. These segments are each nearly planar and have a dihedral angle of 80.1° between them. The internal torsional libration of the anion is physically correlated with its overall external translational and librational motion. Bond distances involving the heavier atoms have an s.u. σ from 0.002 to 0.003 Å while librational corrections in these distances range up to 4σ. A short nonbonded intersegment C···O distance of 2.817 (2) Å becomes 2.831 Å after correction, the correction being 7σ. An intermolecular S···O distance of 3.1891 (14) Å becomes 3.215 Å after correction for independent vibration of the two molecules, the correction being 18σ.

1. Introduction

The reaction of thiophene-2,3-dicarbonyl chloride with $AlCl_3$ and benzene gave 3-benzoyl-2-thiophenecarboxylic acid as one of the products (MacDowell & Ballas, 1977). This acid was then synthesized in order to identify it. The synthesis is now confirmed by the room-temperature crystal structure determination of the potassium salt [(I), Fig. 1]. The results have added interest because the atomic thermal displacement parameters (a.d.p.'s) for the anion have been analyzed in terms of a body having two rigid segments. The internal torsional libration of these segments is found to be physically correlated with the overall rigid-body motion. The thermal libration of the anion gives rise to corrections to the interatomic distances that range up to 7σ.



(I)

2. Experimental

The crystal structure of 3-benzoyl-2-thiophenecarboxylic acid itself could not be determined because this compound crystallizes as fine cotton-like flexible fibrils. The potassium salt of the acid synthesized by MacDowell & Ballas (1977) was prepared by the addition of an aliquot of KOH to the acid in ethanol solution. The salt precipitated and was recrystallized from water. The crystal chosen for X-ray study showed all faces of the forms {001} and {111} so that the crystal shape conformed nearly to the orthorhombic class *mmm*. This facilitated the corrections for X-ray absorption.

Intensity data were collected for two complete octants in reciprocal space. Data collection and cell refinement used *CAD*-4 *Software* (Enraf–Nonius, 1977). The data were merged and average structure amplitudes were

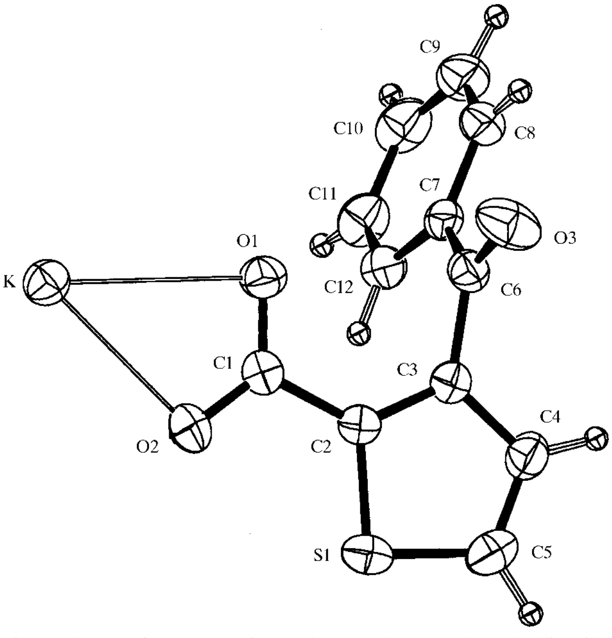


Fig. 1. The atomic configuration and nomenclature. Thermal ellipsoids have 50% probability of enclosing atom centers (Johnson, 1976). For clarity, H atoms are shown as small circles. The view is almost along the *c* axis but with a rotation of 15° about the *b* axis, which is directed across the page.

Table 1. *Experimental details*

Crystal data	
Chemical formula	$KC_{12}H_7O_3S$
Chemical formula weight	270.1
Cell setting	Orthorhombic
Space group	*Pbca*
a (Å)	10.760 (1)
b (Å)	7.740 (1)
c (Å)	27.145 (3)
V (Å^3)	2260.7 (4)
Z	8
D_x (Mg m^{-3})	1.589
Radiation type	Cu $K\alpha$, Ni filtered
Wavelength (Å)	1.5418
No. of reflections for cell parameters	22
θ range (°)	26.0–30.0
μ (mm^{-1})	5.79
Temperature (K)	293
Crystal form	Truncated bipyramid, all faces of forms {001} and {111}
Crystal size (mm)	0.370 × 0.370 × 0.309
Crystal color	Pale yellow
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans
Absorption correction	Analytical integration (Alcock, 1974)
$T_{\rm min}$	0.274
$T_{\rm max}$	0.426
No. of measured reflections	4158
No. of independent reflections	2141
No. of observed reflections	2014
Criterion for observed reflections	$F > \sigma(F)$
$R_{\rm int}$	0.027
$\theta_{\rm max}$ (°)	69.94
Range of h, k, l	$-13 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 9$ $0 \rightarrow l \rightarrow 32$
No. of standard reflections	3
Frequency of standard reflections	Every 50 min
Intensity decay (%)	1
Refinement	
Refinement on	F
R	0.034
wR	0.037
S	2.49
No. of reflections used in refinement	2014
No. of parameters used	183
H-atom treatment	Refined isotropically
Weighting scheme	$w = 1/\sigma^2(F)$; $\sigma^2(I) = \sigma^2(I)_{\rm exp} + 0.02I^2$
$(\Delta/\sigma)_{\rm max}$	0.0003
$\Delta\rho_{\rm max}$ (e Å^{-3})	0.26
$\Delta\rho_{\rm min}$ (e Å^{-3})	−0.33
Extinction method	Becker & Coppens (1974)
Extinction coefficient	$g = 22\ (4) \times 10^4$ rad^{-1}
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1, including $\Delta f'$ for S and K)

used in the structure determination. The space group *Pbca* was established from the observed systematic spectral absences.

The structure was determined straightforwardly by direct methods. All H atoms were located in a difference Fourier synthesis and were included in the refinement. These calculations all used the *Xtal*3.4 software system (Hall *et al.*, 1995). Crystal data and the results of the structure determination are summarized in Table 1 and the atomic parameters are given in Table 2. The subsequent thermal vibration analysis used the *EKRT* program (He & Craven, 1993). The molecular vibration parameters are given in Table 3 and interatomic distances and angles are given in Table 4. Distances with thermal vibration corrections are also given in Table 4.†

3. Discussion

3.1. *Structure description*

Interatomic distances given here (except for C—H) are corrected for thermal vibration (see §3.2). Nonbonded distances are rounded to two decimal places so as not to give a misleading impression of their accuracy.

In the crystal structure, the thiophene and phenyl-ring atoms are each coplanar within experimental error and the two rings make a dihedral angle of 80.1 (1)°. The carboxylate group is nearly coplanar with the thiophene ring and the carbonyl group is nearly coplanar with the phenyl ring. As a consequence, there are short nonbonded distances between the carboxylate O1 atom and the carbonyl C6 atom (2.83 Å) and also between O1 and the phenyl group C7 atom (3.25 Å). It appears that repulsion between the carboxylate and benzoyl groups causes a bending within the plane of the carboxylate group so that the C1—C2—C3 bond angle [128.5 (2)°] is greater than C1—C2—S1 [120.7 (1)°]. In the phenyl ring, corrected C—C bond distances range from 1.375 (3) to 1.400 (2) Å. The range of all C—H bond distances is from 0.92 (2) to 0.97 (2) Å. The K^+ ion is irregularly coordinated by four carboxylate O atoms and one carbonyl O atom at distances from 2.64 to 3.00 Å, and possibly also by an S atom at 3.71 Å. The coordinating atoms come from three surrounding anions. The shortest corrected intermolecular distance is $S1\cdots O2(\frac{1}{2} - x, \frac{1}{2} + y, z)$ at 3.22 (1) Å.

3.2. *Thermal vibration analysis*

From inspection of the thermal ellipsoids (Fig. 1), it is unlikely that the anion is vibrating as a rigid body. Indeed, the rigid-body model (Schomaker & Trueblood, 1968) did not give a good fit to the observed a.d.p.'s

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0064). Services for accessing these data are described at the back of the journal.

Table 2. *Atomic positional and thermal displacement parameters*

(*a*) Fractional positional coordinates and isotropic (for H atoms) or equivalent isotropic displacement parameters (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
K	0.33560 (4)	0.02464 (5)	−0.042742 (15)	0.0386 (2)
S1	0.37341 (4)	0.65858 (6)	0.058823 (19)	0.0398 (2)
C1	0.41217 (15)	0.3135 (2)	0.03443 (6)	0.0313 (8)
C2	0.43791 (14)	0.4598 (2)	0.06870 (7)	0.0294 (8)
C3	0.51328 (15)	0.4623 (2)	0.10929 (6)	0.0299 (8)
C4	0.51837 (18)	0.6268 (2)	0.13223 (8)	0.0402 (10)
C5	0.44638 (19)	0.7447 (2)	0.10861 (9)	0.0449 (11)
O1	0.46176 (12)	0.17154 (16)	0.04483 (5)	0.0401 (7)
O2	0.34303 (11)	0.34482 (18)	−0.00136 (5)	0.0398 (7)
C6	0.58073 (16)	0.3088 (2)	0.12859 (7)	0.0334 (9)
O3	0.69051 (13)	0.2868 (2)	0.11966 (7)	0.0580 (10)
C7	0.51255 (16)	0.1899 (2)	0.16245 (6)	0.0312 (8)
C8	0.5787 (2)	0.0727 (3)	0.19097 (8)	0.0418 (10)
C9	0.5170 (2)	−0.0329 (3)	0.22375 (8)	0.0526 (13)
C10	0.3893 (2)	−0.0253 (3)	0.22773 (9)	0.0522 (13)
C11	0.3228 (2)	0.0880 (3)	0.19922 (8)	0.0463 (11)
C12	0.38375 (17)	0.1966 (2)	0.16683 (7)	0.0358 (9)
H4	0.567 (2)	0.650 (3)	0.1617 (10)	0.061 (7)
H5	0.441 (2)	0.866 (4)	0.1157 (11)	0.072 (8)
H8	0.665 (2)	0.066 (3)	0.1865 (9)	0.043 (6)
H9	0.561 (2)	−0.101 (3)	0.2466 (11)	0.064 (7)
H10	0.346 (2)	−0.095 (4)	0.2506 (12)	0.073 (8)
H11	0.238 (2)	0.081 (3)	0.2027 (9)	0.057 (7)
H12	0.340 (2)	0.279 (3)	0.1473 (8)	0.041 (6)

(*b*) Atomic anisotropic displacement parameters U^{ij} (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K	0.0389 (2)	0.0372 (2)	0.0397 (2)	0.00077 (16)	0.00232 (15)	−0.00196 (16)
S1	0.0401 (2)	0.0358 (2)	0.0436 (3)	0.00701 (18)	0.00028 (19)	0.0082 (2)
C1	0.0297 (8)	0.0362 (9)	0.0282 (8)	−0.0011 (7)	0.0022 (6)	0.0003 (7)
C2	0.0295 (8)	0.0298 (8)	0.0288 (9)	0.0009 (6)	0.0028 (6)	0.0025 (6)
C3	0.0302 (8)	0.0306 (8)	0.0289 (8)	−0.0021 (6)	0.0021 (6)	0.0009 (7)
C4	0.0435 (10)	0.0364 (9)	0.0408 (11)	−0.0023 (8)	−0.0019 (8)	−0.0070 (8)
C5	0.0482 (11)	0.0308 (9)	0.0557 (13)	0.0006 (8)	0.0063 (9)	−0.0042 (9)
O1	0.0474 (7)	0.0349 (6)	0.0379 (7)	0.0077 (5)	−0.0034 (5)	−0.0028 (5)
O2	0.0398 (6)	0.0467 (7)	0.0329 (7)	0.0002 (6)	−0.0071 (5)	0.0005 (6)
C6	0.0337 (8)	0.0355 (9)	0.0311 (9)	0.0025 (7)	−0.0030 (7)	−0.0011 (7)
O3	0.0324 (7)	0.0682 (10)	0.0733 (12)	0.0094 (6)	0.0074 (7)	0.0209 (9)
C7	0.0396 (9)	0.0284 (8)	0.0256 (8)	0.0017 (7)	−0.0033 (7)	−0.0043 (6)
C8	0.0499 (11)	0.0379 (9)	0.0375 (11)	0.0052 (8)	−0.0107 (8)	0.0013 (8)
C9	0.0792 (16)	0.0409 (11)	0.0376 (12)	0.0036 (10)	−0.0140 (10)	0.0104 (9)
C10	0.0771 (15)	0.0413 (11)	0.0382 (12)	−0.0100 (10)	0.0062 (10)	0.0056 (9)
C11	0.0528 (12)	0.0433 (11)	0.0427 (12)	−0.0074 (9)	0.0071 (9)	0.0009 (9)
C12	0.0409 (9)	0.0341 (9)	0.0324 (9)	0.0018 (7)	0.0010 (7)	0.0002 (7)

[$wR(U^{ij})$ = 0.119; goodness-of-fit = 5.27; H atoms excluded]. The relative displacements of covalently bonded atom pairs along the C—C, C—O and C—S bonds were insignificantly different from zero. This is consistent with the rigid motion of such bonded pairs (Harel & Hirshfeld, 1975). However, nonbonded atom pairs gave strong indications of the presence of intramolecular vibrations. Thus, along the intramolecular vector O2$\cdots$O3, these atoms have mean-square displacements differing by 24σ and ten other atom pairs have differences exceeding 8σ. The pattern of differences is consistent with vibrations of the molecular frame as two rigid segments, namely the benzoyl and the 2-thiophenecarboxylate groups with the two segments having torsional motion about the C3—C6 bond. This model was tested using the segmented-body formalism of He & Craven (1993). According to this formalism, an internal vibration occurs with the constraints that the angular and linear momentum of the isolated molecule remain zero throughout (Eckart, 1935). As shown in Fig. 2, all atoms of the anion are moving, including C3 and C6 which lie on the torsion axis. Because of the momentum

Table 3. *Molecular thermal vibration parameters*

Rigid body **T**, **L** and **S** tensor components are given with respect to the axes of the principal moments of inertia of the 3-benzoyl-2-thiophenecarboxylate anion. Components of the internal vibrations are also with respect to the inertial axes. These are in order of decreasing moment of inertia (1621, 1516 and 581 Da Å^2). The origin is at the center of mass.

T (Å^2)	0.0283 (11)	0.0005 (11)	−0.0019 (6)
		0.0235 (13)	−0.0013 (7)
			0.0289 (6)
Principal values	0.0267	0.0232	0.0307
L (°^{2})	7.0 (6)	−0.5 (5)	2.0 (6)
		7.0 (4)	0.7 (7)
			18.2 (10)
Principal values	6.1	7.4	18.6
S (Å °$^{-1}$)	0.02 (3)	0.064 (10)	0.024 (13)
	0.094 (7)	0.04 (3)	−0.008 (12)
	0.04 (3)	0.00 (3)	−0.06
	$j = x$	$j = y$	$j = z$
$<\varphi t_j>$ (° Å^1)	−0.08 (7)	0.39 (6)	−0.12 (4)
$<\varphi\lambda_j>$ (°^{2})	−2.7 (12)	−6.2 (14)	10.9 (11)
$<\varphi\lambda_j>$ (local axes†)	8.2	4.0	9.1

† Cartesian local axes for $<\varphi\lambda_j>$ were chosen with z along the torsion axis C3—C6, and x along the normal to the thiophene plane.

constraints, the internal atomic displacements are dependent on the distribution of atomic masses as well as the atomic positions. The heavy S atom is nearly stationary. The linear displacements (units: Å per degree of torsion) are 0.017 for C3, 0.006 for C6, 0.021 for O1 and 0.024 for O2. Various segmented-body models were tested by trial and error including some with bond-angle bending, but none gave better agreement with the observed U^{ij}'s than the first model.

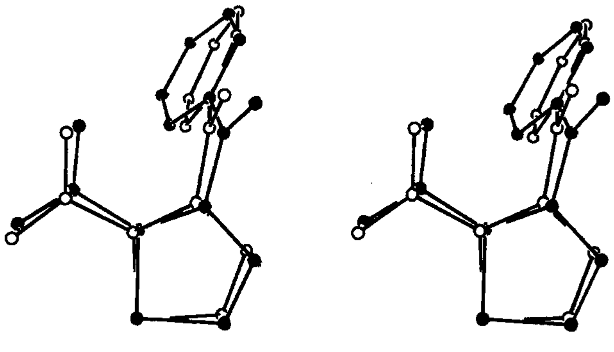

Fig. 2. A stereoview of the anion undergoing internal libration about the C3—C6 axis with an angular amplitude arbitrarily chosen to be φ = 15°. The view is the same as in Fig. 1. The filled atoms represent the anion at one extreme of the libration while the open atoms are at the other. Because this libration is correlated with the overall rigid-body libration about C3—C6, the value of $<\varphi^2>$ cannot be determined from the diffraction data. The amplitude of libration shown here is likely to be exaggerated by about threefold.

Table 4. *Anion interatomic distances (Å) and angles (°)*

(a) Distances in column (1) are before correction for thermal libration and those in (2) are after correction.

	(1)	(2)		(1)	(2)
S1—C2	1.709 (2)	1.714	C3—C6	1.488 (2)	1.491
S1—C5	1.699 (2)	1.708	C6—O3	1.218 (2)	1.224
C2—C3	1.368 (2)	1.374	C6—C7	1.493 (2)	1.499
C3—C4	1.418 (2)	1.425	C7—C8	1.389 (3)	1.392
C4—C5	1.358 (3)	1.361	C8—C9	1.379 (3)	1.384
C1—C2	1.492 (2)	1.499	C9—C10	1.380 (4)	1.387
C1—O1	1.253 (2)	1.257	C10—C11	1.371 (3)	1.375
C1—O2	1.248 (2)	1.252	C11—C12	1.382 (3)	1.387
O1···C6	2.817 (2)	2.831	C12—C7	1.392 (3)	1.400

(b) Selected anion bond angles

C2—S1—C5	92.3 (1)	C4—C3—C6	122.9 (2)
C2—C1—O1	116.5 (2)	C3—C4—C5	112.0 (2)
C2—C1—O2	116.7 (2)	S1—C5—C4	112.1 (2)
O1—C1—O2	126.9 (2)	C3—C6—O3	121.0 (2)
S1—C2—C1	120.7 (1)	C3—C6—C7	118.0 (2)
S1—C2—C3	110.7 (1)	O3—C6—C7	120.9 (2)
C1—C2—C3	128.5 (2)	C6—C7—C8	119.6 (2)
C2—C3—C4	112.9 (2)	C6—C7—C12	121.3 (2)
C2—C3—C6	124.1 (2)	C8—C7—C12	119.1 (2)

The internal libration (amplitude φ) was found to be physically correlated with the overall rigid-body motion. Under these circumstances, $<\varphi^2>$ itself is omitted as a variable and is replaced by the six variables $<\varphi t_j>$ and $<\varphi\lambda_j>$ where t_j and λ_j are the Cartesian components of the rigid-body translation and libration with respect to the inertial axes of the anion. A least-squares fit of the two-segment model to the a.d.p.'s of the anion gave $wR(U^{ij})$ = 0.074 and goodness-of-fit = 3.37. The values obtained for $<\varphi t_y>$, $<\varphi\lambda_y>$ and $<\varphi\lambda_z>$ were very significantly nonzero (Table 3).

Estimation of the librational motion of the anion is important because corrections for thermal vibration can then be applied to the interatomic distances. Dunitz *et al.* (1988) and Schomaker & Trueblood (1998) have pointed out that when the internal and external vibrations are correlated, it is possible to obtain both $<(\varphi + \lambda)^2>$ and $<\lambda^2>$ where λ is the amplitude of overall rigid-body motion about the internal axis, but it is not possible to obtain $<\varphi^2>$ as well. In the present case, for the internal libration about C3—C6, we obtain $<(\varphi + \lambda)^2>$ = 35.3 (14) °^{2} and $<\lambda^2>$ = 17.0 (10) °^{2}. Many of the resulting corrections to the bond distances are substantial (Table 4). For example, the uncorrected S—C bond distances (1.709 and 1.699 Å) have a difference which is significant (3.3σ), but after corrections (1.714 and 1.708 Å) the difference has only marginal significance (2.0σ). The intersegment nonbonded distance O1···C7 increases from 3.242 (2) to 3.254 Å after correction. This is a difference of 6σ. The unusually short intramolecular distance O1···C6 increases from 2.817 (2) to 2.831 Å after correction. This is a difference of 7.0σ.

Intermolecular nonbonded distances may also require substantial vibrational corrections. Busing & Levy (1964) gave a series of corrections to obtain a mean interatomic distance from the experimentally determined distance between thermally averaged atom centers. The correction depends on the assumed joint distribution for the two vibrating atoms. Busing & Levy (1964) report (i) the minimum possible correction, (ii) the riding mode correction, (iii) the correction for uncorrelated motion, and (iv) the maximum possible correction. Correction (iii) is appropriate for van der Waals distances between atoms in molecules that are vibrating with only weak interactions. In the crystal structure of the title thiophene derivative, there is a short intermolecular distance $S1\cdots O2(\frac{1}{2} - x, \frac{1}{2} + y, z)$ of 3.1891 (14) Å which becomes 3.215 Å after correction for uncorrelated vibration. The difference is 18σ.

Vibrational corrections are difficult to estimate for the ionic $K\cdots O$ interactions. Values of the difference in mean-square displacements $U_K - U_O$ along the $K\cdots O$ vectors are in the range -5 to $+13\sigma$ for the five nearest-neighbor O atoms. Therefore the central K and its nearest neighbors are not vibrating rigidly. Assuming that the O atoms are riding on K, corrections to the $K\cdots O$ distances are in the range 0.001 to 0.009 Å. Corrections assuming uncorrelated motion are in the range 0.025 to 0.034 Å. The most likely correction would be between these limits. In §3.1, we report the range of $K\cdots O$ distances with an estimated correction of 0.01 Å.

In conclusion we repeat an earlier caution (Busing & Levy, 1964) that it can be misleading to report uncorrected interatomic distances with the precision now routinely available from a structure determination. The mean interatomic distances that are of chemical interest may be significantly longer, particularly for weaker nonbonded interactions.

BMC is grateful to the faculty and administration at Indiana University of Pennsylvania for their role in establishing a new X-ray laboratory. This work is the first to come entirely from that facility.

References

Alcock, N. W. (1974). *Acta Cryst.* A**30**, 332–335.

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Dunitz, J. D., Schomaker, V. & Trueblood, K. N. (1988). *J. Chem. Phys.* **92**, 856–867.

Eckart, C. (1935). *Phys. Rev.* **47**, 552–558.

Enraf–Nonius (1977). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.

Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). *Xtal3.4 User's Manual.* Perth: Lamb Printers.

Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* B**31**, 162–172.

He, X.-M. & Craven, B. M. (1993). *Acta Cryst.* A**49**, 10–22.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

MacDowell, D. W. H. & Ballas, F. L. (1977). *J. Org. Chem.* **42**, 3717–3720.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Schomaker, V. & Trueblood, K. N. (1998). *Acta Cryst.* B**54**, 507–514.