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## Synthesis and Structure of Strained Polycyclic Cyclobutane-Containing Derivatives

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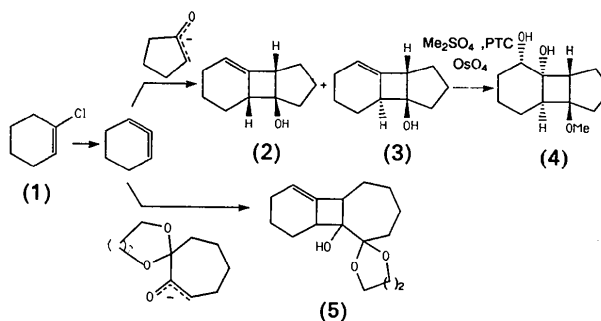
### Abstract

The compounds *cis,anti,cis*-8-methoxytricyclo[6.3.0.-0<sup>2,7</sup>]undecan-2,3-diol and *cis,anti,cis*-tricyclo[6.5.0.0<sup>2,7</sup>]-tridec-6-en-13-spiro-2'-[1,3]dioxan-1-ol were obtained

by condensation of ketone enolates with cyclohexadiene generated *in situ* from 1-chlorocyclohexene. X-ray structure analysis established the conformations of the polycyclic systems, the stereochemistry at the ring junctions and the deformations caused by fusion of the rings. The results of the refinements on *F* and *F*<sup>2</sup> are compared.

### Comment

It was shown for the first time in a work by Caubère & Brunet (1972) that condensation of a ketone enolate with cyclohexadiene, generated *in situ* from 1-chlorocyclohexene, leads easily to the synthesis of a methylene cyclobutenol with *cis,syn,cis* structure. Returning to these reactions with the object of finding a new route to polycyclic cyclopentane derivatives, we performed the reactions shown in the scheme below (PTC = phase transfer catalysis).



Compound (3) has not been obtained previously and its formation can be attributed to the new experimental conditions used here (a temperature lower than 273 K and dimethoxyethane). It was first transformed into the corresponding ether which was bishydroxylated into compound (4) (Minato, Yamamoto & Tsuji, 1990) whose structure could only be established by X-ray analysis. Using this knowledge, it was possible to infer the structure of (3).

Another reaction we considered was the condensation of the enolate of cycloheptanedione monoketal; although this reaction is much less easy than arynic condensation (Grégoire, Carré & Caubère, 1986), we succeeded in obtaining compound (5) whose stereochemistry could not be determined easily from classical spectroscopic data and was therefore defined by X-ray analysis.

The present paper reports the structures of compounds (4) and (5) which are good starting materials for further transformations (Jamart-Grégoire, Brosse, Caubère, Ianelli & Nardelli, 1991), for example those of (5) into the rearranged polycyclic derivatives we are currently investigating.

The *ORTEP* (Johnson, 1965) projections (Fig. 1) show that both molecules are built up of a tricyclic core with an *anti* conformation and with *cis* configurations at the

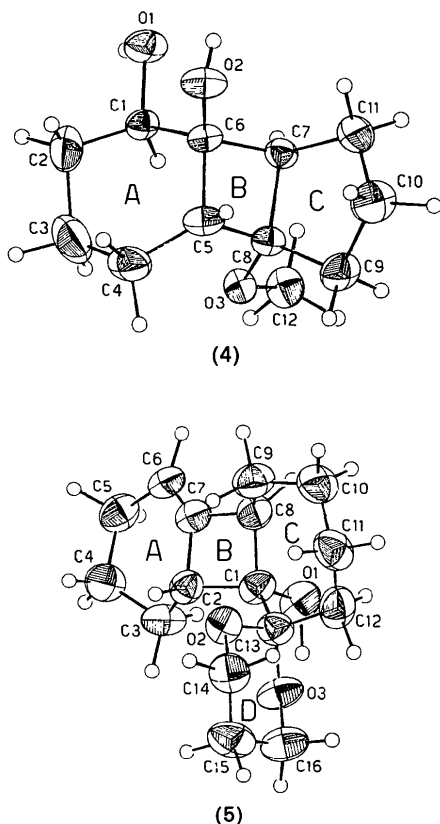


Fig. 1. ORTEP projections of the two molecules. Ellipsoids are drawn at the 40% level for (4) and the 50% level for (5).

junctions. In compound (5), a dioxane residue is spiro-joined to the cycloheptane ring at the C atom adjacent to the hydroxyl-substituted junction.

There are four chiral centers in (4) [configurations  $R(C5)$ ,  $R(C6)$ ,  $R(C7)$ ,  $R(C8)$ ] and three in (5) [configurations  $S(C1)$ ,  $R(C2)$ ,  $R(C8)$ ]. In the latter, the enantiomorph is also present since the space group is centrosymmetric; the configurations quoted for the former must be considered only to be relative as the absolute configuration has not been established.

The values of bond distances and angles quoted in Table 2 are as expected, apart from C3—C4 in (4) [1.407 (12) Å] which is too short, probably as a result of the apparent contraction caused by the high anisotropic thermal motion (or static disorder) of C3 ( $U_{eq} = 0.129$  Å<sup>2</sup>). This distance increases to 1.548 Å if the correction for non-correlated motion (Busing & Levy, 1964) is applied. The anisotropy of the displacement is expressed well by the ratio  $r_{max}/r_{min} (= 5.17)$  of the maximum and minimum principal axes of the ellipsoid.

The relevant conformational features of the rings, together with the dihedral angles formed by the mean planes through the rings are compared in Table 3. The presence of the double bond in the six-membered alkene ring of (5)

reduces its puckering; a comparison with the corresponding values in (4) reveals its influence on the angles and distances of the joined cyclobutane ring.

The system formed by a dioxane residue spiro-joined to a cycloheptane ring, present in (5), is quite similar to the one we described recently (Ianelli *et al.*, 1992). In particular, it is worth noting the narrowing of the angle C1—C13—C12 and the chair conformation of the cycloheptane ring with the local pseudo-symmetry plane running through C11 and the midpoint of the C1—C8 junction.

The orientation of the methoxy group in (4) is determined mainly by the steric hindrance between the methyl H atoms and the C9 methylene group or the C7—H7 and C1—H1 H atoms when the methoxy group is rotated about the C8—O3 bond.

The orientation of the hydroxyl groups in (4) is determined by the hydrogen-bonding interactions in which these groups are involved. An intermolecular hydrogen bond is formed by O1—H1 [O1—H1 0.85 (3), O1...O2<sup>i</sup> 2.890 (4), H1...O2<sup>i</sup> 2.04 (3) Å, O1—H1...O2<sup>i</sup> 180 (1)°; symmetry code: (i)  $-x, \frac{1}{2} + y, -1 - z$ ] and a bifurcated intra-intermolecular hydrogen bond by O2—H2 [O2—H2 0.85 (2), O2...O1 2.722 (4), H2...O1 2.41 (2) Å, O2—H2...O1 102 (1)°; O2...O3<sup>ii</sup> 2.941 (4), H2...O3<sup>ii</sup> 2.11 (2) Å, O2—H2...O3<sup>ii</sup> 165 (2)°; symmetry code: (ii)  $x, y, z - 1$ ].

There is no condition for intermolecular hydrogen bonding in (5) so the molecular packing is determined only by van der Waals interactions. The O1—H1 hydroxyl group is involved in an intramolecular interaction with one O atom of the dioxane moiety [O1—H1 0.85 (3), O1...O3 2.607 (3), H1...O3 2.25 (3) Å, O1—H1...O3 106 (2)°].

For all these hydrogen bonds, minima are found in the potential-energy profiles which correspond to the orientations observed in the crystal when only the van der Waals and Coulombic energies (Hagler, Huler & Lifson, 1974; Dauber & Hagler, 1980) are considered, assuming fractional point charges of  $-0.6$  and  $+0.5$  e for the O and H atoms, respectively.

Analysis of the anisotropic atomic displacements was carried out in terms of the LST rigid-body model according to Schomaker & Trueblood (1968) and Trueblood (1978) using the program THMV (Trueblood, 1984). This gave values for the residual index  $R_{wU}$  of 0.183 [0.176] and 0.081 [0.100] for compounds (4) and (5), respectively [ $R_{wU} = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{1/2}$ ;  $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$ ]. (In each case, the first figure refers to the  $U$  values derived from the refinement on  $F^2$  and that in square brackets to values derived from the refinement on  $F$ .) The values of this index improve to 0.090 [0.097] for (4) and 0.073 [0.089] for (5) if internal motions are considered according to Dunitz & White (1973). These findings are related to the fact that (unconcerted) anisotropies are more relevant in the former compound ( $r_{max}/r_{min} = 1.61-5.17$  [1.54-4.23], average 2.70 [2.67])

than in the latter ( $r_{\max}/r_{\min} = 1.33\text{--}2.90$  [1.37–3.16], average 1.94 [2.06]).

## Experimental

### Compound (4)

#### Crystal data

$C_{12}H_{20}O_3$   
 $M_r = 212.29$   
 Monoclinic  
 $P2_1$   
 $a = 8.573$  (1) Å  
 $b = 10.628$  (1) Å  
 $c = 6.544$  (1) Å  
 $\beta = 105.55$  (1)°  
 $V = 574.4$  (1) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.228$  Mg m<sup>-3</sup>

#### Data collection

Siemens-AED diffractometer  
 $\theta$ -2 $\theta$  scans  
 1242 measured reflections  
 1152 independent reflections  
 864 observed reflections  
 [ $I > 2\sigma(I)$ ]  
 $R_{\text{int}} = 0.0086$   
 $\theta_{\text{max}} = 69.96^\circ$   
 Cu  $K\alpha$  mean radiation for  
 collection of intensity data

#### Refinement

Refinement on  $F^2$   
 Final  $R1 = 0.0486$  for  
 $F_o > 4\sigma(F_o)$   
 $wR2 = 0.1219$  for  $F^2$  data  
 $S = 1.049$  for all  $F^2$  data  
 1147 reflections  
 143 parameters  
 Only H-atom  $U$ 's refined  
 Calculated weights  
 $w = 1/[\sigma^2(F_o^2) + (0.0830P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = -0.020$

### Compound (5)

#### Crystal data

$C_{16}H_{24}O_3$   
 $M_r = 264.36$   
 Monoclinic  
 $P2_1/c$   
 $a = 8.394$  (1) Å  
 $b = 14.260$  (2) Å  
 $c = 12.007$  (1) Å  
 $\beta = 91.79$  (1)°  
 $V = 1436.5$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.22$  Mg m<sup>-3</sup>

Cu  $K\alpha_1$  radiation  
 $\lambda = 1.540562$  Å  
 Cell parameters from 30  
 reflections  
 $\theta = 25\text{--}30^\circ$   
 $\mu = 0.662$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Small prisms  
 $0.36 \times 0.33 \times 0.27$  mm  
 Colorless

$h = -10 \rightarrow 10$   
 $k = 0 \rightarrow 12$   
 $l = 0 \rightarrow 7$   
 1 standard reflection  
 monitored every 50  
 reflections  
 intensity variation: within  
 statistical fluctuation

$\Delta\rho_{\text{max}} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>  
 Extinction correction:  
 $F_c^* = kF_c[1 + 0.001F_c^2\lambda^3$   
 $/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient:  
 0.0350 (44)  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallogra-*  
*phy* [1974, Vol. IV, Tables  
 2.2A, 2.3.1 (O, C) and  
 2.2C (H)]

Cu  $K\alpha_1$  radiation  
 $\lambda = 1.540562$  Å  
 Cell parameters from 30  
 reflections  
 $\theta = 21\text{--}39^\circ$   
 $\mu = 0.622$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Small prisms  
 $0.43 \times 0.40 \times 0.36$  mm  
 Colorless

#### Data collection

Siemens-AED diffractometer  
 $\theta$ -2 $\theta$  scans  
 2924 measured reflections  
 2739 independent reflections  
 1476 observed reflections  
 [ $I > 2\sigma(I)$ ]  
 $R_{\text{int}} = 0.0055$   
 $\theta_{\text{max}} = 70.54^\circ$   
 Cu  $K\alpha$  mean radiation for  
 collection of intensity data

#### Refinement

Refinement on  $F^2$   
 Final  $R1 = 0.0603$  for  
 $F_o > 4\sigma(F_o)$   
 $wR2 = 0.1635$  for  $F^2$  data  
 $S = 1.064$  for all  $F^2$  data  
 2715 reflections  
 177 parameters  
 Only H-atom  $U$ 's refined  
 Calculated weights  
 $w = 1/[\sigma^2(F_o^2) + (0.1144P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.000$

$h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 17$   
 $l = -14 \rightarrow 14$   
 1 standard reflection  
 monitored every 50  
 reflections  
 intensity variation: within  
 statistical fluctuation

$\Delta\rho_{\text{max}} = 0.267$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.164$  e Å<sup>-3</sup>  
 Extinction correction:  
 $F_c^* = kF_c[1 + 0.001F_c^2\lambda^3$   
 $/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient:  
 0.0008 (6)  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallogra-*  
*phy* [1974, Vol. IV, Tables  
 2.2A, 2.3.1 (O, C) and  
 2.2C (H)]

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å<sup>2</sup>)

For non-H atoms  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
(4)				
O1	-0.0440 (4)	-0.00039	-0.5287 (5)	0.0681 (13)
O2	-0.0970 (4)	-0.2530 (4)	-0.5635 (4)	0.0566 (11)
O3	-0.2271 (3)	-0.1341 (4)	0.0197 (4)	0.0469 (8)
C1	-0.0211 (5)	-0.0685 (5)	-0.3374 (5)	0.0450 (11)
C2	0.1541 (6)	-0.1020 (7)	-0.2315 (8)	0.0812 (21)
C3	0.1534 (9)	-0.1584 (9)	-0.0116 (12)	0.1290 (34)
C4	0.0585 (6)	-0.2672 (7)	-0.0197 (8)	0.0819 (21)
C5	-0.1007 (5)	-0.2713 (5)	-0.1886 (6)	0.0485 (13)
C6	-0.1236 (5)	-0.1877 (4)	-0.3866 (5)	0.0400 (12)
C7	-0.3004 (4)	-0.1611 (5)	-0.3853 (6)	0.0465 (13)
C8	-0.2606 (4)	-0.2189 (4)	-0.1567 (5)	0.0422 (11)
C9	-0.3922 (7)	-0.3152 (5)	-0.1571 (7)	0.0678 (18)
C10	-0.4487 (8)	-0.3580 (7)	-0.3880 (8)	0.0937 (26)
C11	-0.4375 (6)	-0.2427 (8)	-0.5176 (7)	0.0821 (20)
C12	-0.3526 (5)	-0.0483 (6)	0.0255 (7)	0.0611 (16)
H1	-0.0026 (66)	0.0724 (21)	-0.5020 (11)	0.082 (12)
H2	-0.1245 (60)	-0.2064 (19)	-0.6729 (18)	0.082 (12)
(5)				
O1	0.8710 (2)	0.8432 (2)	0.3257 (2)	0.0724 (8)
O2	0.4829 (2)	0.8450 (1)	0.1891 (2)	0.0609 (6)
O3	0.5719 (2)	0.8242 (2)	0.3733 (2)	0.0727 (7)
C1	0.7599 (3)	0.8343 (2)	0.2350 (2)	0.0575 (9)
C2	0.7646 (3)	0.7364 (2)	0.1784 (2)	0.0584 (9)
C3	0.8316 (4)	0.6495 (2)	0.2342 (3)	0.0747 (12)
C4	0.8924 (4)	0.5851 (2)	0.1415 (3)	0.0799 (12)
C5	1.0262 (4)	0.6304 (2)	0.0764 (3)	0.0717 (11)
C6	1.0024 (3)	0.7328 (2)	0.0574 (2)	0.0622 (10)
C7	0.8816 (3)	0.7774 (2)	0.0998 (2)	0.0571 (10)
C8	0.8440 (3)	0.8771 (2)	0.1328 (2)	0.0602 (9)
C9	0.7524 (4)	0.9388 (2)	0.0523 (3)	0.0778 (13)
C10	0.7140 (5)	1.0354 (2)	0.0996 (3)	0.0852 (14)
C11	0.5820 (4)	1.0366 (2)	0.1834 (3)	0.0815 (13)
C12	0.6013 (4)	0.9773 (2)	0.2875 (3)	0.0754 (12)

C13	0.5983 (3)	0.8720 (2)	0.2708 (2)	0.0579 (9)	(5)			
C14	0.3222 (3)	0.8595 (2)	0.2231 (3)	0.0716 (12)	Ring A	0.517 (3)	$\Delta_2$ (C3—C4) = 0.060 (1)	Half-chair $A^{\wedge}B = 155.5$ (5)
C15	0.2922 (4)	0.8062 (3)	0.3270 (3)	0.0848 (13)	B	0.050 (1)	—	$B^{\wedge}C = 148.4$ (1)
C16	0.4141 (4)	0.8318 (3)	0.4148 (3)	0.0850 (14)	C	0.775 (3)	$\Delta_5$ (C11) = 0.067 (1)	Chair $A^{\wedge}C = 166.2$ (1)
H1	0.8388 (2)	0.8119 (2)	0.3808 (2)	0.120 (16)	D	0.523 (3)	—	Chair $C^{\wedge}D = 115.6$ (1)

Table 2. Geometric parameters (Å, °)

(4)			
O1—C1	1.414 (5)	C5—C6	1.539 (6)
O2—C6	1.419 (5)	C5—C8	1.545 (6)
O3—C8	1.431 (5)	C6—C7	1.545 (6)
O3—C12	1.419 (6)	C7—C8	1.567 (5)
C1—C2	1.518 (6)	C7—C11	1.529 (7)
C1—C6	1.526 (6)	C8—C9	1.523 (7)
C2—C3	1.560 (10)	C9—C10	1.527 (7)
C3—C4	1.41 (1)	C10—C11	1.508 (10)
C4—C5	1.509 (5)		
C8—O3—C12	115.9 (3)	C1—C6—C7	110.9 (4)
O1—C1—C6	107.6 (3)	O2—C6—C7	117.8 (3)
O1—C1—C2	114.2 (3)	C6—C7—C11	120.0 (4)
C2—C1—C6	110.2 (4)	C6—C7—C8	88.3 (3)
C1—C2—C3	105.3 (4)	C8—C7—C11	104.8 (4)
C2—C3—C4	115.3 (6)	C5—C8—C7	89.2 (3)
C3—C4—C5	116.8 (6)	O3—C8—C7	117.9 (3)
C4—C5—C8	123.5 (3)	O3—C8—C5	110.0 (3)
C4—C5—C6	119.1 (4)	C7—C8—C9	106.9 (3)
C6—C5—C8	89.3 (3)	C5—C8—C9	116.2 (4)
C1—C6—C5	111.4 (3)	O3—C8—C9	114.4 (3)
O2—C6—C5	113.1 (3)	C8—C9—C10	103.9 (4)
O2—C6—C1	111.7 (3)	C9—C10—C11	105.3 (5)
C5—C6—C7	90.3 (3)	C7—C11—C10	107.3 (4)
(5)			
O1—C1	1.418 (3)	C4—C5	1.531 (5)
O2—C13	1.410 (3)	C5—C6	1.490 (4)
O2—C14	1.436 (3)	C6—C7	1.314 (4)
O3—C13	1.431 (3)	C7—C8	1.511 (4)
O3—C16	1.434 (4)	C8—C9	1.501 (4)
C1—C2	1.554 (4)	C9—C10	1.528 (5)
C1—C8	1.559 (4)	C10—C11	1.520 (5)
C1—C13	1.533 (4)	C11—C12	1.513 (5)
C2—C3	1.509 (4)	C12—C13	1.515 (4)
C2—C7	1.501 (4)	C14—C15	1.488 (5)
C3—C4	1.542 (5)	C15—C16	1.492 (5)
C13—O2—C14	113.2 (2)	C2—C7—C8	93.2 (2)
C13—O3—C16	115.6 (2)	C1—C8—C7	86.7 (2)
O1—C1—C13	108.7 (2)	C7—C8—C9	119.4 (2)
O1—C1—C8	105.5 (2)	C1—C8—C9	120.0 (2)
O1—C1—C2	113.0 (2)	C8—C9—C10	113.6 (3)
C8—C1—C13	120.7 (2)	C9—C10—C11	115.0 (3)
C2—C1—C13	118.2 (2)	C10—C11—C12	118.6 (3)
C2—C1—C8	89.3 (2)	C11—C12—C13	116.4 (3)
C1—C2—C7	87.2 (2)	C1—C13—C12	111.9 (2)
C1—C2—C3	123.9 (2)	O3—C13—C12	111.2 (2)
C3—C2—C7	110.9 (2)	O3—C13—C1	103.7 (2)
C2—C3—C4	107.2 (3)	O2—C13—C12	111.8 (2)
C3—C4—C5	112.5 (3)	O2—C13—C1	107.7 (2)
C4—C5—C6	113.3 (3)	O2—C13—O3	110.3 (2)
C5—C6—C7	121.1 (3)	O2—C14—C15	110.5 (2)
C2—C7—C6	125.7 (3)	C14—C15—C16	109.7 (3)
C6—C7—C8	136.6 (3)	O3—C16—C15	110.9 (3)

Table 3. Relevant conformational parameters (Å, °) of the rings in the two compounds

$Q_T$  is the total puckering amplitude (Cremer & Pople, 1975) and DAP the displacement asymmetry parameter (Nardelli, 1983b).

(4)	$Q_T$	DAP	Conformation	Dihedral angle
Ring A	0.544 (6)	$\Delta_2$ (C1—C2) = 0.033 (2)	Half-chair	$A^{\wedge}B = 125.9$ (2)
B	0.045 (1)	—	—	$B^{\wedge}C = 111.9$ (2)
C	0.334 (6)	$\Delta_2$ (C7) = 0.009 (2)	Envelope	$A^{\wedge}C = 156.6$ (2)

The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. A correction was applied for Lorentz and polarization effects but not for absorption. The intensity data of compound (5) were corrected for decay.

Both structures were determined by direct methods with *SHELXS86* (Sheldrick, 1986) and refined by anisotropic full-matrix least squares on *F* using *SHELXL76* (Sheldrick, 1976) and on  $F^2$  (to have a better ratio between the numbers of observations and refined parameters) using *SHELXL92* (Sheldrick, 1992). In the refinement on *F*, the H atoms in both compounds were placed at calculated positions, riding on the C atoms to which they were attached, except for the hydroxy H atoms which were refined isotropically. The H atoms were placed at calculated positions in the  $F^2$  refinement. The values of the conventional residual-error indices at the end of the *F* refinements were  $R = 0.0493$ ,  $wR = 0.0671$  for 869 data and 191 parameters for compound (4) and  $R = 0.0644$ ,  $wR = 0.0609$  for 1495 data and 238 parameters for (5). These compare well with the final  $R1 = [\sum |F_o - F_c| / \sum F_o]$  indices obtained in the  $F^2$  refinements [compound (4):  $wR2 = \{\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]\}^{1/2} = 0.1219$  for 1147 data (five reflections with  $\Delta/\sigma > 4$  omitted) and 143 parameters,  $wR2 = 0.1384$  for all 1152 data,  $S = 0.944$ ,  $R1 = 0.0486$  for 864  $F_o > 4\sigma(F_o)$ ; compound (5):  $wR2 = 0.1635$  for 2715 data (19 reflections with  $\Delta/\sigma > 5$  omitted) and 177 parameters,  $wR2 = 0.2305$  for all 2734 data,  $S = 0.883$ ,  $R1 = 0.0603$  for 1476  $F_o > 4\sigma(F_o)$ ].

As expected, the e.s.d.'s from the  $F^2$  analyses are lower than those from the analyses on *F* as a result of the larger number of observations and the reduced number of parameters. A further comparison of the results obtained from the two types of analysis is provided by the half-normal probability plots (Abrahams & Keve, 1971); these were calculated using the program *ABRAHAMS* (Gilli, 1977) for all interatomic distances  $< 4.65$  Å (excluding those involving H atoms) according to De Camp (1973) (Figs. 2a and 2b) and for the  $U_{eq}$  values (Figs. 2c and 2d). The relevant parameters of the regression lines through the distributions of points in the two plots for each of the two structures are given below ( $i$  = intercept,  $s$  = slope,  $r$  = correlation coefficient,  $N$  = number of observations):

Compound	Fig.	$i$	$s$	$r$	$N$
(4)	2(a)	-0.09 (2)	0.89 (2)	0.982	93
	2(c)	-0.10 (9)	0.93 (9)	0.939	15
	2(b)	0.05 (2)	1.67 (2)	0.995	123
(5)	2(d)	0.12 (3)	0.71 (3)	0.981	19

It is apparent from the plots in Fig. 2 that the e.s.d.'s of  $U_{eq}$  are overestimated, particularly for compound (5), while the e.s.d.'s on the distances are overestimated by a factor of about 0.9 for compound (4) and underestimated by a factor of about 1.7 for (5). In neither case are significant differences (*i.e.*  $> 3\Delta/\sigma$ ) observed between the structural parameters (distances, angles, torsions) derived from the two analyses.

With regard to the comparison of the  $U_{eq}$  values, it is interesting that in the case of compound (4), the  $U_{eq}(F^2)$  values are systematically greater than  $U_{eq}(F)$ ; the differences are generally less than  $\sigma = [\sigma^2(U_F) + \sigma^2(U_{F^2})]^{1/2}$ , the only exception being for

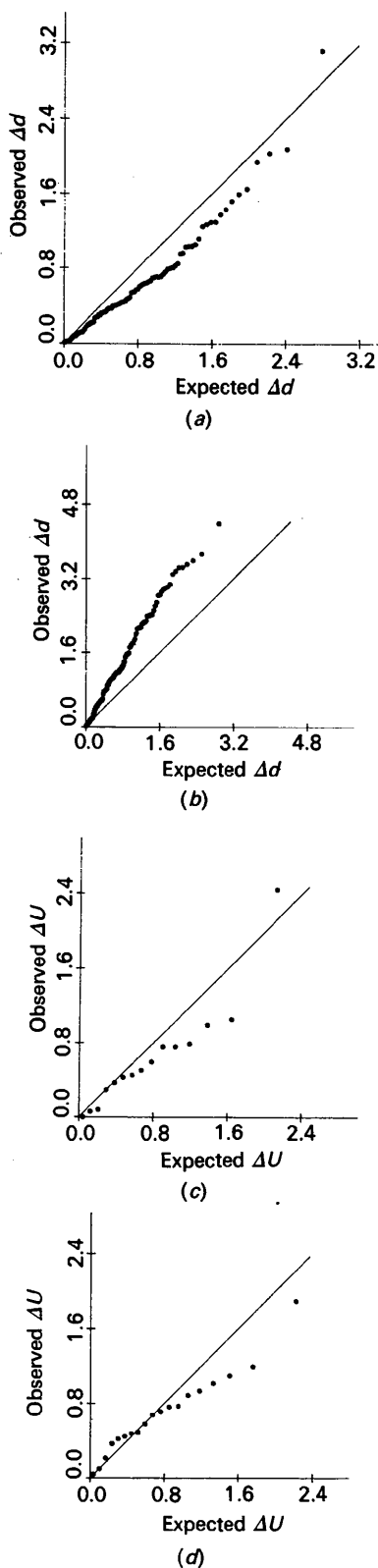


Fig. 2. Half-normal probability plots comparing the results of the refinements on  $F$  and  $F^2$ : (a) distances in (4), (b) distances in (5), (c)  $U_{eq}$ 's in (4) and (d)  $U_{eq}$ 's in (5).

the disordered atom C3 where the difference is  $\sim 2.4\sigma$ . Some systematic effect is also present for (5), the intercept being a little greater than zero.

All the structural parameters discussed in the *Comment* are from the  $F^2$  refinements.

The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffattometrica del CNR (Parma). Material was prepared for publication using *PARST* (Nardelli, 1983a).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71019 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1032]

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