

Acta Cryst. (1973). B29, 2617**2,4,6-Trimethyl-3-pivaloylbenzoic Acid**

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Abstract. $C_{15}H_{20}O_3$, triclinic, $P\bar{1}$, $a=11.337$ (2), $b=6.149$ (2), $c=11.932$ (2) Å, $\alpha=100.74$ (2), $\beta=109.39$ (1), $\gamma=104.97$ (2)°, $Z=2$, $D_x=1.14$ g cm⁻³. The structure shows no evidence of steric strain, the mean planes through the ketone group and the acid group making angles of 89.9 and 81.7° respectively with the mean plane of the six-membered ring.

Introduction. Crystals of the compound (Fig. 1) are colourless, transparent plates elongated on the chosen crystallographic b axis and with (100) developed, the dimensions of the crystal chosen for data collection being $0.3 \times 0.3 \times 0.1$ mm. The intensities of the reflexions were measured on a Datex-automated General Electric XRD 6 diffractometer with Cu $K\alpha$ radiation. With $2\theta \leq 146^\circ$, 2223 reflexions were measured of which 1412 (63.5%) had intensities greater than 3σ above background, where $\sigma(I)$ is defined by $\sigma^2(I) = S + B + (0.03S)^2$; S is the scan count and B the background count. Lorentz and polarization factors were

applied. The E -statistics of the data indicated the centrosymmetric space group $P\bar{1}$ and it seemed reasonable to assume a structure in which centrosymmetric acid dimers were linked by hydrogen bonds between the carboxyl groups across the unit-cell origin. With the use of this assumption the coordinates of ten of the fifteen carbon atoms were deduced from a three-dimensional Patterson function and the remainder of the non-hydrogen atoms were located from subsequent electron-density maps. After full-matrix least-squares anisotropic refinement of these atoms, nineteen of the twenty hydrogen atoms were located from a difference synthesis; the hydrogen of the carboxylic acid group could not be located. Refinement continued with the

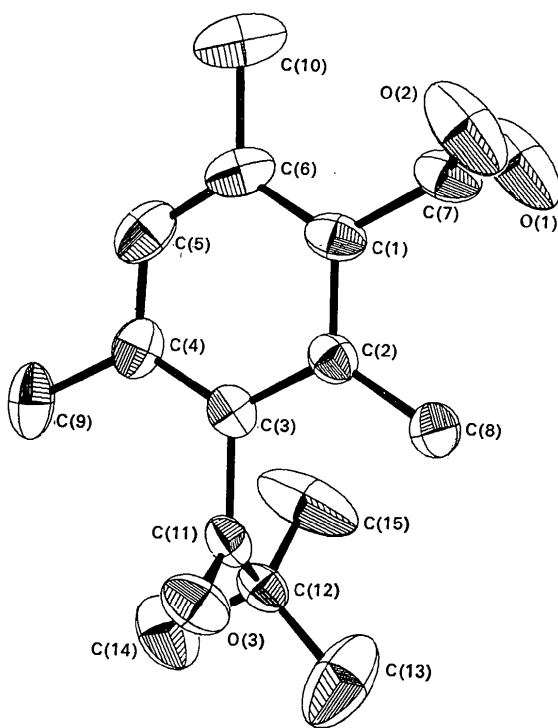


Fig. 1. The structure of 2,4,6-trimethyl-3-pivaloylbenzoic acid; the ellipsoids enclose 25% probability.

Table 1. *Final positional and thermal* (Å²) *parameters*

| | x/a | y/b | z/c | B_{iso} |
|--------|-------------|--------------|-------------|-----------|
| C(1) | 0.1103 (4) | 0.1324 (8) | 0.7781 (4) | |
| C(2) | 0.2187 (4) | 0.0732 (7) | 0.7702 (4) | |
| C(3) | 0.2649 (4) | 0.1375 (7) | 0.6815 (4) | |
| C(4) | 0.2015 (5) | 0.2438 (8) | 0.5995 (4) | |
| C(5) | 0.0943 (6) | 0.2923 (10) | 0.6113 (6) | |
| C(6) | 0.0472 (5) | 0.2475 (9) | 0.6990 (6) | |
| C(7) | 0.0640 (4) | 0.0739 (9) | 0.8755 (5) | |
| C(8) | 0.2793 (6) | -0.0600 (12) | 0.8494 (6) | |
| C(9) | 0.2437 (10) | 0.3022 (13) | 0.4976 (6) | |
| C(10) | -0.0696 (9) | 0.3167 (19) | 0.7065 (16) | |
| C(11) | 0.3867 (5) | 0.0856 (8) | 0.6743 (4) | |
| C(12) | 0.5254 (4) | 0.2717 (8) | 0.7508 (4) | |
| C(13) | 0.6145 (11) | 0.1538 (30) | 0.8175 (18) | |
| C(14) | 0.5834 (11) | 0.3680 (22) | 0.6654 (9) | |
| C(15) | 0.5211 (10) | 0.4762 (25) | 0.8380 (15) | |
| O(1) | 0.1179 (5) | 0.2085 (10) | 0.9815 (4) | |
| O(2) | -0.0331 (5) | -0.1006 (9) | 0.8479 (5) | |
| O(3) | 0.3733 (4) | -0.0981 (6) | 0.6078 (4) | |
| H(51) | 0.047 (5) | 0.378 (10) | 0.555 (5) | 8 (1) |
| H(81) | 0.328 (8) | -0.119 (15) | 0.825 (8) | 14 (3) |
| H(82) | 0.340 (8) | 0.048 (15) | 0.931 (8) | 13 (2) |
| H(83) | 0.219 (7) | -0.201 (13) | 0.859 (6) | 13 (2) |
| H(91) | 0.309 (9) | 0.464 (17) | 0.523 (8) | 15 (3) |
| H(92) | 0.295 (6) | 0.196 (13) | 0.477 (6) | 11 (2) |
| H(93) | 0.174 (6) | 0.284 (10) | 0.427 (6) | 9 (2) |
| H(101) | -0.130 (9) | 0.222 (15) | 0.721 (7) | 12 (3) |
| H(102) | -0.036 (10) | 0.414 (18) | 0.793 (9) | 16 (3) |
| H(103) | -0.103 (7) | 0.377 (13) | 0.657 (7) | 22 (2) |
| H(131) | 0.592 (9) | 0.129 (17) | 0.893 (9) | 17 (3) |
| H(132) | 0.710 (11) | 0.245 (17) | 0.860 (8) | 15 (3) |
| H(133) | 0.586 (7) | -0.011 (13) | 0.761 (6) | 19 (2) |
| H(141) | 0.685 (7) | 0.497 (12) | 0.727 (6) | 10 (2) |
| H(142) | 0.573 (6) | 0.213 (12) | 0.612 (7) | 11 (2) |
| H(143) | 0.511 (7) | 0.442 (12) | 0.619 (7) | 18 (2) |
| H(151) | 0.469 (8) | 0.429 (12) | 0.882 (7) | 12 (2) |
| H(152) | 0.602 (7) | 0.569 (13) | 0.878 (6) | 11 (2) |
| H(153) | 0.473 (7) | 0.541 (13) | 0.796 (7) | 21 (3) |

Table 1 (cont.)

| | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-------|-----------|------------|------------|------------|-----------|-------------|
| C(1) | 0.055 (2) | 0.069 (3) | 0.093 (3) | 0.009 (2) | 0.035 (2) | 0.008 (2) |
| C(2) | 0.061 (2) | 0.068 (2) | 0.066 (2) | 0.014 (2) | 0.029 (2) | 0.016 (2) |
| C(3) | 0.074 (3) | 0.055 (2) | 0.069 (3) | 0.014 (2) | 0.032 (2) | 0.014 (2) |
| C(4) | 0.086 (3) | 0.062 (3) | 0.082 (3) | 0.016 (2) | 0.022 (3) | 0.029 (2) |
| C(5) | 0.092 (4) | 0.084 (4) | 0.118 (5) | 0.033 (3) | 0.018 (4) | 0.047 (3) |
| C(6) | 0.068 (3) | 0.074 (3) | 0.133 (5) | 0.032 (3) | 0.030 (3) | 0.025 (3) |
| C(7) | 0.054 (2) | 0.081 (3) | 0.096 (4) | 0.001 (2) | 0.033 (2) | -0.005 (3) |
| C(8) | 0.087 (3) | 0.099 (4) | 0.091 (4) | 0.040 (3) | 0.049 (3) | 0.051 (3) |
| C(9) | 0.147 (6) | 0.094 (4) | 0.076 (4) | 0.027 (5) | 0.032 (4) | 0.045 (3) |
| C(10) | 0.085 (5) | 0.122 (6) | 0.240 (14) | 0.051 (4) | 0.057 (7) | 0.046 (8) |
| C(11) | 0.091 (3) | 0.066 (3) | 0.068 (3) | 0.027 (2) | 0.049 (2) | 0.024 (2) |
| C(12) | 0.072 (3) | 0.087 (3) | 0.084 (3) | 0.018 (2) | 0.048 (2) | 0.022 (3) |
| C(13) | 0.102 (6) | 0.214 (14) | 0.244 (15) | 0.016 (7) | 0.015 (8) | 0.148 (13) |
| C(14) | 0.121 (6) | 0.158 (8) | 0.140 (7) | -0.001 (6) | 0.079 (6) | 0.045 (7) |
| C(15) | 0.088 (5) | 0.183 (10) | 0.215 (12) | -0.044 (7) | 0.081 (7) | -0.104 (11) |
| O(1) | 0.142 (4) | 0.162 (4) | 0.117 (3) | -0.068 (3) | 0.076 (3) | -0.035 (3) |
| O(2) | 0.155 (4) | 0.126 (4) | 0.121 (4) | -0.047 (3) | 0.086 (3) | -0.024 (3) |
| O(3) | 0.124 (3) | 0.075 (2) | 0.118 (3) | 0.029 (2) | 0.069 (2) | 0.010 (2) |

hydrogen atoms included and being refined with isotropic temperature factors, and terminated at an R value of 0.083 for the observed reflexions with $I \leq 3\sigma(I)$ (0.115 for all reflexions). The relatively high final R value is probably a result of poor quality of the crystal specimen.

Final values of the positional and temperature parameters are listed in Table 1, with bond lengths and angles given in Table 2.*

Discussion. In the course of investigations into restricted rotation about the carbonyl group in ketones by the use of dipole moment measurements (Pinkus &

Custard, 1970) it had been found that 2,4,6-trimethyl-3-pivaloylbenzoic acid racemizes fairly rapidly in solution (Pinkus, Riggs & Broughton, 1968), although models indicate that rotation of the *t*-butyl group is not possible. In order to shed some light on this problem the crystal structure analysis of the compound was undertaken.

The mean planes (Table 3) through the six-membered ring, the acid group, and the ketone group show that the latter two groups are almost orthogonal to the benzene ring. The ketone group makes an angle of 89.9° with the ring, in agreement with a value assumed for *t*-butyl mesityl ketone (Pinkus & Custard, 1970). The angle that the acid group makes with the ring, 81.7°, however, shows an increase over the value of 48.5° found in 2,4,6-trimethylbenzoic acid by an X-ray analysis (Florenco & Smith, 1970). However, in the latter compound the methyl groups *ortho* to the acid group show an in-plane deformation which gives a slight increase in the valence angles to 124.2 and 123.3°. In the present study while this deformation may possibly be present for C(10) with an angle of 122.9 (9)°, it is not present at C(8) because of the interaction with the ketone group, but there is a slight out-of-plane deformation of 4.4° for C(8). It seems unlikely, however, that this small variation in itself can account for the fairly large increase (33.2°) in the angle between the ring and the acid group. Nevertheless it is of some significance that C(8) is fairly rigidly held, as shown by the higher thermal parameters of C(9) and C(10) compared with C(8), and these features would, if anything, support a contention that racemization should not occur.

A possible explanation for the racemization is in the bending of the *t*-butyl group away from the ring, thereby increasing the C-CO-C angle (Pinkus, Riggs & Broughton, 1968). It has been calculated (Pinkus & Custard, 1970) that in methyl *t*-butyl ketone the C-CO-C angle is increased from the value of 116° (Swalen & Costain, 1959) of unhindered dialkyl ketones to 121°. In 2,4,6-trimethyl-3-pivaloylbenzoic

* A table of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30178 (21 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) and angles (°) for non-hydrogen atoms

| | | | |
|-----------------|-----------|-------------------|------------|
| C(1)-C(2) | 1.395 (6) | C(5)-C(6) | 1.365 (8) |
| C(1)-C(6) | 1.402 (7) | C(6)-C(10) | 1.518 (9) |
| C(1)-C(7) | 1.490 (7) | C(7)-O(1) | 1.222 (6) |
| C(2)-C(3) | 1.403 (6) | C(7)-O(2) | 1.221 (6) |
| C(2)-C(8) | 1.478 (7) | C(11)-C(12) | 1.531 (6) |
| C(3)-C(4) | 1.384 (7) | C(11)-O(3) | 1.194 (5) |
| C(3)-C(11) | 1.521 (6) | C(12)-C(13) | 1.496 (12) |
| C(4)-C(5) | 1.367 (8) | C(12)-C(14) | 1.497 (10) |
| C(4)-C(9) | 1.515 (8) | C(12)-C(15) | 1.513 (9) |
| C(2)-C(1)-C(6) | 121.7 (4) | C(1)-C(6)-C(10) | 122.9 (9) |
| C(2)-C(1)-C(7) | 118.0 (5) | C(5)-C(6)-C(10) | 120.4 (9) |
| C(6)-C(1)-C(7) | 120.2 (4) | C(1)-C(7)-O(1) | 120.0 (4) |
| C(1)-C(2)-C(3) | 117.6 (4) | C(1)-C(7)-O(2) | 120.0 (4) |
| C(1)-C(2)-C(8) | 121.1 (4) | O(1)-C(7)-O(2) | 119.8 (5) |
| C(3)-C(2)-C(8) | 121.3 (4) | C(3)-C(11)-C(12) | 119.5 (3) |
| C(2)-C(3)-C(4) | 121.8 (4) | C(3)-C(11)-O(3) | 119.9 (4) |
| C(2)-C(3)-C(11) | 119.0 (4) | C(12)-C(11)-O(3) | 120.6 (4) |
| C(4)-C(3)-C(11) | 119.3 (4) | C(11)-C(12)-C(13) | 108.1 (6) |
| C(3)-C(4)-C(5) | 117.3 (5) | C(11)-C(12)-C(14) | 110.1 (5) |
| C(3)-C(4)-C(9) | 123.1 (6) | C(11)-C(12)-C(15) | 111.8 (4) |
| C(5)-C(4)-C(9) | 119.6 (6) | C(13)-C(12)-C(14) | 107.1 (10) |
| C(4)-C(5)-C(6) | 124.8 (6) | C(13)-C(12)-C(15) | 112.4 (12) |
| C(1)-C(6)-C(5) | 116.7 (5) | C(14)-C(12)-C(15) | 107.3 (10) |

Table 3. Equations of mean planes and deviations (Å) of relevant atoms from the planes

$X, Y,$ and Z are in Å referred to orthogonal axes $a, b',$ and c^* .

| | | | | | | | |
|---|--------|-------|--------|-------------------|--------|-------|--------|
| Plane (1): C(1)–C(6) | | | | | | | |
| $-0.204X - 0.730Y - 0.652Z + 3.697 = 0$ | | | | | | | |
| C(1) | -0.001 | C(2) | 0.015 | C(3) | -0.018 | C(4) | 0.009 |
| C(5) | 0.019 | C(6) | -0.021 | C(7) | -0.023 | C(8) | 0.113 |
| C(9) | 0.058 | C(10) | -0.055 | C(11) | -0.065 | C(12) | -1.420 |
| C(13) | -1.403 | C(14) | -1.621 | C(15) | -2.557 | | |
| Plane (2): C(3), C(11), C(12), O(3) | | | | | | | |
| $0.080X + 0.650Y - 0.756Z + 6.484 = 0$ | | | | | | | |
| C(3) | 0.002 | C(11) | -0.006 | C(12) | 0.002 | O(3) | 0.002 |
| Plane (3): C(1), C(7), O(1), O(2) | | | | | | | |
| $-0.759X + 0.611Y - 0.226Z + 1.461 = 0$ | | | | | | | |
| C(1) | 0.005 | C(7) | -0.023 | O(1) | 0.009 | O(2) | 0.010 |
| Angles between planes | | | | | | | |
| | | | | Plane(1)–plane(2) | 89.9° | | |
| | | | | Plane(1)–plane(3) | 81.7 | | |

acid with the more bulky trimethylbenzoic acid group one would expect an even larger value; however, this particular angle is found to be 119.5 (3)°. This does not preclude the possibility that this angle may increase in the racemization process in solution.

The carboxylic acid group has an unusual feature in that both the C–O lengths are equal, within the limits of error. This is possibly due to disorder, where some of the molecules have crystallized with the acid group rotated through approximately 180° with respect to the other molecules; the elongation of the oxygen thermal ellipsoids in the direction of rotation thus possibly results from non-coincidence of the two orientations. As the molecules form hydrogen-bonded dimers the orientation of one half of the dimer necessarily fixes the orientation of the other half. The O...O distance is 2.642 Å.

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2-(3'-Bromophenyl)-4-acetoxy-6H-1,3-oxazin-6-one

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Abstract. C₁₂H₈NO₄Br; M.W. 310.12; monoclinic, space group, $P2_1/c$; $a = 8.490$ (2), $b = 16.797$ (2), $c = 8.381$ (1) Å, $\beta = 95.09$ (1)°; $D_m = 1.716$ g cm⁻³; $D_c = 1.732$ g cm⁻³ for $Z = 4$. Mo $K\alpha$ diffractometer data. $R = 0.035$. The identification of the N and O atoms in

the oxazinone ring is described. Bond lengths show evidence for an α -pyrone type of resonance interaction.

Introduction. A preliminary X-ray diffraction study of the 2-phenyl derivative *Ia* showed that the compound crystallized in the orthorhombic space group $Fdd2$. Since a phase solution in this acentric space group could be difficult, we turned our attention to the *m*-bromophenyl derivative, *Ib*, which crystallized from

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