$C_{20}H_{60}FN_5Si_9$

Fig. 1. A view of the molecule showing the atom numbering and torsion angles (°) for the ring bonds. Torsion angles have an e.s.d. of 0·2°. The sign convention is that of Klyne & Prelog (1960).

$(SiMe_2.NSiMe_3)_3$, which has bulky substituents, is also non-planar (Adamson & Daly, 1970).

The Si—N lengths cover a wide range [1·698 (3) to 1·776 (3) Å]. The shortest are those involving Si(7), which is bonded to an electronegative F atom, and those which are exocyclic to the four-membered ring. This shortening of Si—N bonds exocyclic to Si_2N_2 rings appears to be general (Wheatley, 1962; Clegg,

Klingebiel, Krampe & Sheldrick, 1980; Clegg, Klingebiel & Sheldrick, 1980).

All N atoms have essentially planar coordination, as is usual in such compounds (Bürger, 1973).

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The Structure of Benzoin

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Abstract. $C_{14}H_{12}O_2$, m.p. 409–410 K, monoclinic, $P2_1/a$, $a = 18·76$ (2), $b = 5·765$ (5), $c = 10·44$ (2) Å, $\beta = 107·1$ (2)°, $D_m = 1·29$, $D_x = 1·307$ Mg m^{-3}, $Z = 4$. The structure was refined to $R = 0·082$ for 1820 non-zero reflexions. Molecules related by a 2_1 axis are linked together by bifurcated hydrogen bonds to form columns along b. The columns are held together by van der Waals interactions along a and c. The keto group makes a dihedral angle of 12·0 (1)° with the plane of the phenyl ring attached to it. The dihedral angle between the two terminal phenyl rings is 64·5 (1)°. The torsion angle O=C—C—O is 26·0 (4)°. The O···O distance is 2·585 (4) Å, but there is no intramolecular hydrogen bond between the O atoms.

Introduction. The present work forms part of a study on the relationship between molecular conformation and crystal structure for aromatic compounds in which two benzene rings are separated by two bonding atoms. It has been shown previously that when the two bonding atoms are different the two benzene rings usually make a dihedral angle of about 60° (Kashino, Ito & Haisa, 1979). The molecular conformation of benzoin is of particular interest because of its ability to form intramolecular hydrogen bonds in solution (Joris & Schleyer, 1968), and its use as a chelating agent (Koester & Rotermund, 1965). The unit-cell dimensions have been obtained (Prasad & Shanker, 1936), but the crystal structure has not been determined.

Crystals obtained from an ethanol solution were prisms elongated along b and bounded by {100}, {001} and {$\bar{2}$01}. Intensity data were collected on Weissenberg photographs with crystals 0·4 × 2·1 × 0·3 mm for the layers $h0l$ to $h4l$, and 0·5 × 0·5 × 0·4 mm for the layers $hk0$ to $hk8$. Visually estimated intensities were corrected for Lorentz and polarization factors and for spot shape, but no absorption correction was made [μ(Cu $K\alpha$) = 0·70 mm^{-1}]. Intensities of 1820 non-zero
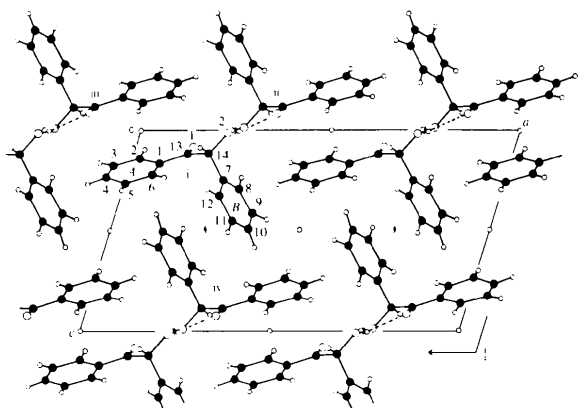

Fig. 1. Projection of the crystal structure along b, and numbering of the non-hydrogen atoms. Broken lines indicate hydrogen bonds. Symmetry code: (i) x,y,z; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (iii) $-x,-y,-z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

Table 1. *Final atomic parameters (positional* ×10⁴, *for* H ×10³) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq} or B_{iso} (Å²)
O(1)	1528 (1)	−3037 (3)	818 (2)	3·90 (9)
O(2)	2310 (1)	158 (4)	129 (2)	3·38 (8)
C(1)	753 (1)	−584 (5)	1624 (2)	2·49 (10)
C(2)	202 (1)	−2285 (5)	1383 (3)	2·98 (11)
C(3)	−445 (2)	−1909 (6)	1748 (3)	3·76 (13)
C(4)	−543 (2)	145 (7)	2356 (4)	4·29 (14)
C(5)	6 (2)	1822 (6)	2612 (4)	4·14 (14)
C(6)	650 (2)	1473 (5)	2232 (3)	3·34 (12)
C(7)	2544 (1)	1090 (4)	2509 (3)	2·58 (9)
C(8)	3058 (1)	−682 (5)	2975 (3)	3·12 (11)
C(9)	3598 (2)	−453 (6)	4196 (3)	3·87 (13)
C(10)	3628 (2)	1509 (6)	4977 (3)	3·95 (14)
C(11)	3111 (2)	3257 (6)	4525 (3)	3·89 (13)
C(12)	2576 (2)	3061 (5)	3284 (3)	3·25 (11)
C(13)	1421 (1)	−1085 (4)	1163 (3)	2·45 (9)
C(14)	1973 (1)	841 (4)	1122 (3)	2·59 (9)
H(1)	27 (2)	−370 (5)	97 (3)	0·4 (5)
H(2)	−84 (2)	−316 (7)	161 (4)	3·3 (9)
H(3)	−98 (2)	31 (7)	269 (4)	3·5 (9)
H(4)	−3 (2)	321 (7)	300 (4)	3·5 (9)
H(5)	99 (2)	267 (6)	239 (3)	1·6 (7)
H(6)	302 (2)	−218 (7)	237 (4)	2·7 (8)
H(7)	401 (2)	−167 (7)	446 (4)	3·1 (9)
H(8)	392 (2)	172 (8)	579 (4)	4·1 (10)
H(9)	312 (2)	462 (8)	512 (4)	3·9 (10)
H(10)	222 (2)	433 (7)	294 (4)	3·0 (9)
H(11)	259 (2)	142 (6)	0 (3)	1·5 (6)
H(12)	170 (2)	225 (5)	85 (3)	0·2 (5)

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

O(1)·C(13)	1·216 (4)	C(11)−C(12)	1·391 (5)
O(2)−C(14)	1·419 (4)	C(13)−C(14)	1·527 (4)
C(1)−C(2)	1·393 (4)	O(2)—H(11)	0·93 (4)
C(1)·C(6)	1·385 (4)	C(2)−H(1)	0·95 (3)
C(1)−C(13)	1·497 (4)	C(3) H(2)	1·01 (4)
C(2)−C(3)	1·392 (4)	C(4)−H(3)	0·99 (4)
C(3)·C(4)	1·381 (5)	C(5) H(4)	0·91 (4)
C(4)−C(5)	1·380 (6)	C(6)−H(5)	0·92 (4)
C(5)−C(6)	1·393 (5)	C(8)−H(6)	1·06 (4)
C(7) C(8)	1·391 (4)	C(9)· H(7)	1·02 (4)
C(7) C(12)	1·386 (4)	C(10) H(8)	0·87 (5)
C(7)−C(14)	1·534 (4)	C(11)· H(9)	1·00 (5)
C(8)−C(9)	1·382 (5)	C(12)−H(10)	0·98 (4)
C(9)−C(10)	1·386 (6)	C(14)−H(12)	0·96 (3)
C(10)−C(11)	1·382 (6)		
C(2)−C(1)−C(6)	119·3 (3)	C(1) C(2) H(1)	120 (2)
C(2) C(1)· C(13)	116·9 (3)	C(3) C(2)· H(1)	120 (2)
C(6)−C(1)−C(13)	123·7 (3)	C(2)−C(3) H(2)	121 (2)
C(1) C(2)−C(3)	120·1 (3)	C(4)· C(3) H(2)	119 (2)
C(2)−C(3)· C(4)	120·3 (3)	C(3)−C(4) H(3)	119 (2)
C(3)−C(4) C(5)	119·8 (4)	C(5)−C(4) H(3)	121 (2)
C(4)−C(5)· C(6)	120·3 (4)	C(4)−C(5) H(4)	124 (3)
C(1)−C(6) C(5)	120·3 (3)	C(6)−C(5) H(4)	116 (3)
C(8)−C(7) C(12)	119·4 (3)	C(1)·C(6)· H(5)	123 (3)
C(8)−C(7)· C(14)	118·8 (3)	C(5)−C(6) H(5)	117 (3)
C(12) C(7)−C(14)	121·8 (3)	C(7) C(8)··H(6)	118 (2)
C(7) C(8)−C(9)	119·8 (3)	C(9)· C(8)··H(6)	122 (2)
C(8) C(9)−C(10)	120·8 (4)	C(8) C(9)· H(7)	118 (2)
C(9)−C(10)−C(11)	119·4 (4)	C(10)·· C(9)−H(7)	120 (2)
C(10)· C(11) ·C(12)	120·0 (4)	C(9) C(10)−H(8)	126 (3)
C(7)−C(12) ·C(11)	120·4 (3)	C(11)−C(10)−H(8)	114 (3)
O(1)−C(13)−C(1)	120·0 (3)	C(10)−C(11)−H(9)	119 (3)
O(1)−C(13) C(14)	119·5 (3)	C(12) C(11)−H(9)	121 (3)
C(1)−C(13)−C(14)	120·5 (3)	C(7)··C(12)−H(10)	119 (3)
O(2) C(14)−C(7)	112·2 (2)	C(11)−C(12)·· H(10)	120 (2)
O(2)−C(14) C(13)	105·7 (2)	O(2)··C(14)−H(12)	109 (2)
C(7) C(14)−C(13)	109·4 (2)	C(7)−C(14)−H(12)	111 (2)
C(14)−O(2)−H(11)	106 (2)	C(13)−C(14)· H(12)	108 (2)

reflexions (74% of the reflexions within the Cu $K\alpha$ sphere) were placed on an approximately absolute scale by Wilson's plot ($B = 3·5$ Å²).

The structure was solved by a symbolic-addition procedure. The H atoms were located from a difference Fourier map. The refinements were made by block-diagonal least-squares calculations. The weighting scheme during the later stages was: $w = 1·0$ for $0 < |F_o| \le 8·0$, $w = (8·0/|F_o|)^2$ for $|F_o| > 8·0$. The final R was 0·082 for the non-zero reflexions. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Computations were carried out at the Okayama University Computer Center. The programs used were *SIGM, TANG, HBLS*-5 and *DAPH* (Ashida, 1973), and *MOLCON* (Fujii, 1979).

The final atomic parameters are listed in Table 1.* A projection of the crystal structure viewed along b is

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35468 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Least-squares planes and displacements* (Å)
of atoms

$$X = ax + cz \cos \beta, \ Y = by, \ Z = cz \sin \beta.$$

(1) Keto group

$$-0.265X + 0.215Y - 0.940Z + 1.838 = 0$$

O(1)*	0.000 (4)	C(1)*	0.000 (4)	C(14)*	0.000 (4)
C(13)	0.000 (4)	C(2)	0.269 (5)	C(6)	-0.214 (6)
O(2)	0.598 (5)	C(7)	-1.441 (5)		

(2) Phenyl group (*A*)

$$0.185X - 0.404Y + 0.896Z - 1.756 = 0$$

C(1)*	0.001 (4)	C(2)*	0.004 (4)	C(3)*	-0.002 (4)
C(4)*	-0.005 (5)	C(5)*	0.010 (5)	C(6)*	-0.004 (4)
C(13)	-0.038 (5)	C(14)	-0.329 (6)	O(1)	0.165 (6)

(3) Phenyl group (*B*)

$$0.783X + 0.432Y - 0.447Z - 2.285 = 0$$

C(7)*	0.001 (4)	C(8)*	-0.005 (4)	C(9)*	0.007 (5)
C(10)*	0.003 (5)	C(11)*	-0.012 (5)	C(12)*	0.006 (4)
C(14)	0.052 (5)				

* Atoms used for the calculation of the planes.

shown in Fig. 1. Bond lengths and angles are given in Table 2, and the displacements of atoms from the least-squares planes in Table 3.

Discussion. In the crystals molecules related by a 2_1 axis are linked together by bifurcated hydrogen bonds $|O(2^i) \cdots O(1^{ii})$ 2.842 (4), $H(11^i) \cdots O(1^{ii})$ 2.10 (4) Å, $O(2^i)-H(11^i) \cdots O(1^{ii})$ 136 (3), $H(11^i) \cdots O(1^{ii})-C(13^{ii})$ 119 (1)°; $O(2^i) \cdots O(2^{ii})$ 3.000 (4), $H(11^i) \cdots O(2^{ii})$ 2.17 (4) Å, $O(2^i)-H(11^i) \cdots O(2^{ii})$ 148 (3), $H(11^i) \cdots O(2^{ii})-C(14^{ii})$ 113 (1)°| to form columns along *b*. The columns are held together along *a* and *c* by van der Waals interactions between molecules (i) and (iii), and (i) and (iv). The energies are estimated to be −21.4 and −17.2 kJ mol⁻¹, respectively, from the universal potential of Kitaigorodsky (1973), in agreement with the morphology of the crystals. The phenyl ring (A^i) attached to the carbonyl group overlaps with (A^{iii}) related to it by Ī. The interplanar distance is 3.51 Å, short contacts being $C(3^i) \cdots C(13^{iii})$ 3.506 (4) and $C(1^i) \cdots C(2^{iii})$ 3.535 (4) Å. The dihedral angle of 85.3 (1)° between the rings (A^i) and (B^{iv}) is close to that found in benzene. The angle between rings (B^i) and (B^{iv}) is 51.1 (1)°. The cooperative interaction of the hydrogen bonding around the 2_1 axis with the overlapping of the phenyl rings (A) related by Ī results in the $P2_1/a$ structure.

The molecule is composed of three planes: the keto group and phenyl groups (A) and (B), Table 3. The torsion angle τ_1 $|C(2)-C(1)-C(13)-O(1)|$ is −12.5 (4)°, which favours conjugation. The angle τ_2

$|O(1)-C(13)-C(14)-O(2)|$, 26.0 (4)°, and thus τ_3 $|C(1)-C(13)-C(14)-C(7)|$, 84.9 (3)°, are determined by the intermolecular hydrogen bonding. This small τ_2 results in a short $O(1) \cdots O(2)$ distance, 2.585 (3) Å, but there is no intramolecular hydrogen bond between the O atoms. The conformation corresponding to τ_3 is *trans* in related compounds which have no intermolecular hydrogen bonding: $\tau_3 = 175.4°$ for deoxyanisoin (Norment & Karle, 1962) and 179.9° for phenyl benzoate (Adams & Morsi, 1976). The conformation around the C(14)−C(7) bond corresponds to *gauche*, τ_4 $|C(13)-C(14)-C(7)-C(8)|$ being 68.9 (3)°, and τ_5 $|O(2)-C(14)-C(7)-C(8)|$ −48.1 (4)°. The conformations around the exocyclic bonds described above result in a dihedral angle of 64.5 (1)° between the two phenyl rings (A) and (B). A calculation made by assuming the universal potential of Kitaigorodsky (1973) shows that the energy of the intramolecular van der Waals interactions between the two rings takes a minimum value of −4.2 kJ mol⁻¹ at the observed conformation. The relationship between the carbonyl C=O length and the *s* character of the C atom found for ketones (Kashino & Haisa, 1977) also holds for benzoin.

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