(Roedig & Märkl, 1960) and which gives the same acetate on treatment with potassium carbonate and acetic anhydride (Strömberg *et al.*, 1987). The direct formation of (3*b*) from (1) probably proceeds through anhydride-initiated cyclization of the intermediate (2).

The two crystallographically independent (3*b*) molecules (Fig. 1) are virtually identical. The five-membered ring is planar to within experimental error in the primed molecule, and planar to within 0·030 (8) Å in the unprimed molecule. The molecular geometry (Table 2) is normal, with mean distances $C(sp^2)—Cl = 1{\cdot}685\ (7)$, $C(sp^3)—Cl = 1{\cdot}760\ (9)$, $C{=}O = 1{\cdot}182\ (4)$, $C(sp^2)—O = 1{\cdot}379\ (11)$, $C(sp^3)—O = 1{\cdot}413\ (12)$, $C{=}C = 1{\cdot}302\ (8)$, $C(sp^2)—C(sp^2) = 1{\cdot}475\ (13)$, $C(sp^2)—C(sp^3) = 1{\cdot}50\ (2)$, and $C(sp^3)—C(sp^3) = 1{\cdot}535\ (1)$ Å. There are possible weak C—H···O hydrogen bonds involving the H atoms of the dichloromethyl groups: C(7)—H(7)···O(4′) ($\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$) and C(7′)—H(7′)···O(4) ($1-x, -y, 1-z$) [H···O = 2·40, 2·41 Å; C···O = 3·311 (9), 3·23 (1) Å; C—H···O = 155, 141°]. The shortest intermolecular distance between non-hydrogen atoms is Cl(1′)···O(2) = 3·045 (6) Å.

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Structure–Reactivity Correlations of Benzoin Alkyl Ethers. Structures of 2-Methoxy-1,2-diphenylethanone (I) and 2-Isopropoxy-1,2-diphenylethanone (II)

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Abstract. (I): $C_{15}H_{14}O_2$, $M_r = 226{\cdot}27$, triclinic, $P\bar{1}$, $a = 8{\cdot}441\ (2)$, $b = 10{\cdot}276\ (1)$, $c = 15{\cdot}342\ (2)$ Å, $\alpha = 91{\cdot}02\ (2)$, $\beta = 79{\cdot}26\ (2)$, $\gamma = 105{\cdot}88\ (2)°$, $V = 1256{\cdot}8\ (4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}209$ (flotation in KI), $D_x = 1{\cdot}195$ g cm^{-3}, $\mu(\text{Mo}, \lambda = 0{\cdot}7107$ Å$) = 0{\cdot}44$ cm^{-1}, $F(000) = 480$, $T = 293$ K, $R = 0{\cdot}060$ for 1793 significant reflections. (II): $C_{17}H_{18}O_2$, $M_r = 254{\cdot}83$, orthorhombic, $Pca2_1$, $a = 8{\cdot}476\ (1)$, $b = 16{\cdot}098\ (3)$, $c = 10{\cdot}802\ (3)$ Å, $V = 1473{\cdot}9\ (5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}161$ (flotation in KI), $D_x = 1{\cdot}148$ g cm^{-3}, $\mu(\text{Mo}, \lambda = 0{\cdot}7107$ Å$) = 0{\cdot}41$ cm^{-1}, $F(000) = 544$, $T = 293$ K, $R = 0{\cdot}071$ for 867 significant reflections. Both (I) and (II) crystallize in a *cisoid* conformation for the carbonyl group and alkoxy groups. Compounds (I) and (II) are photostable on irradiation in the solid state in spite of the favourable conformation of the functional groups for intramolecular H abstraction. Absence of photoreaction of (I) and (II) in the solid state is rationalized in the light of unfavourable intramolecular geometry.

Introduction. Photolysis of benzoin alkyl ethers (I)–(III) in solution has been studied extensively (Tomioka & Izawa, 1980) and these were found to undergo only α-cleavage (Norrish type I) to form a benzoyl–benzyl radical pair which subsequently undergoes a free-radical reaction to give pinacol ethers and benzil as main products together with minor amounts of benzaldehyde. Irradiation of crystalline benzoin ethers results in no reaction. When the benzoin alkyl ethers were enclosed in a cyclodextrin cavity (β or γ) significant results were obtained on irradiation in the solid state. Under these conditions in all three cases products resulting from type I were absent whereas type II products were obtained in near quantitative yield (Dasaratha Reddy, Usha, Ramanathan & Ramamurthy, 1986). It has been suggested that the lack of type II products on irradiation of crystalline (I)–(III) is because of the absence of suitable conformers favourable for type II. Therefore crystallographic work

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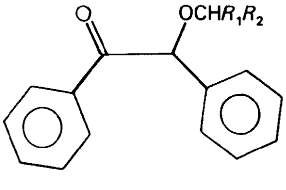
was undertaken to understand the photostability of benzoin ethers and photoreactivity of cyclodextrin complexes of (I)–(III). The present paper describes the crystal and molecular structures of (I) and (II).



(I) $R_1 = R_2 = H$
(II) $R_1 = R_2 = CH_3$
(III) $R_1 = H, R_2 = CH_3$

Experimental. Single crystals of (I) and (II) obtained from ligroin and ethyl acetate respectively by slow evaporation, approximate dimensions 0·2 × 0·1 × 0·9 mm (I) and 0·4 × 0·2 × 0·5 mm (II). Preliminary Weissenberg photographs indicated triclinic (I) and orthorhombic (II) symmetry. The crystals of (II) were not diffracting very well. Lattice parameters from a least-squares fit to settings of 25 accurately centred reflections for both (I) and (II). Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed of 1° $\min^{-1}$, $\theta \leq 24{\cdot}0°$ [for (I) and (II)]. Three monitored standard reflections (233, 442, 215) for (I) and two (193, 314) for (II) showed only statistical variations within ±4%. 3747 (I) and 1456 (II) total reflections of which 1793 (I) and 867 (II) were significant, $|F_o| \geq 3\sigma(|F_o|)$; *hkl* range *h*: 0 to 9, *k*: −11 to 11, *l*: −17 to 17 for (I) and *h*: 0 to 9, *k*: 0 to 18, *l*: 0 to 12 for (II). No correction for absorption. Structures solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement (*SHELX*76; Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, fixed stereochemically and verified from difference maps) converged to $R = 0{\cdot}060$, $wR = 0{\cdot}069$, $S = 0{\cdot}80$ for (I) and $R = 0{\cdot}071$, $wR = 0{\cdot}077$, $S = 1{\cdot}28$ for (II); $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1{\cdot}000/[\sigma^2(F) + 0{\cdot}004391|F|^2]$ for (I) and $1{\cdot}9043/[\sigma^2(F) + 0{\cdot}000972|F|^2]$ for (II). Δ/σ for non-H atoms = 0·04 (I) and 0·06 (II); Δ/σ for H atoms 0·012 (I) and 0·015 (II); $\Delta\rho_{\max} = +0{\cdot}20$, $\Delta\rho_{\min} = -0{\cdot}32$ e Å^{-3} for (I) and $\Delta\rho_{\max} = +0{\cdot}28$, $\Delta\rho_{\min} = 0{\cdot}25$ e Å^{-3} for (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. There are two molecules in the asymmetric unit of compound (I), designated as molecules *A* and *B*. A perspective view and numbering scheme for molecules *A*, *B* and (II) are shown in Figs. 1–3. Positional coordinates of non-H atoms of (I) and (II)

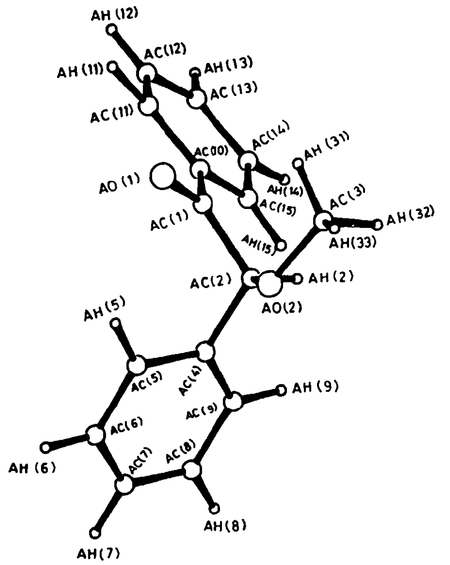


Fig. 1. Atom numbering for molecule *A* of compound (I).

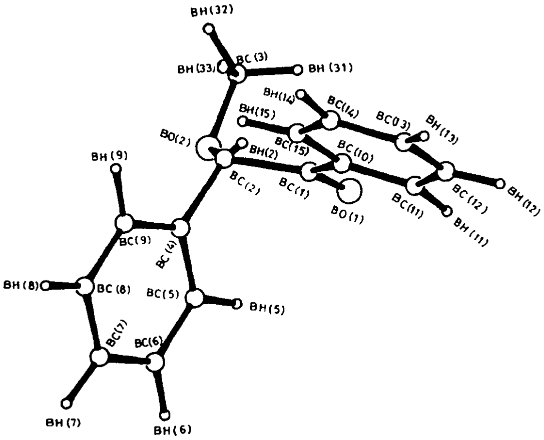


Fig. 2. Atom numbering for molecule *B* of compound (I).

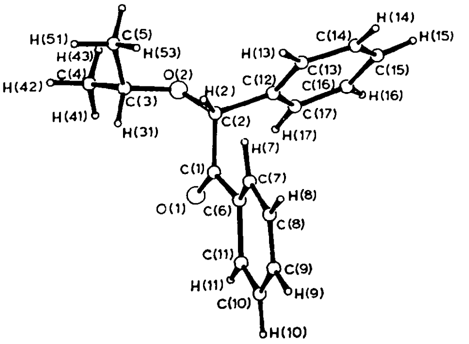


Fig. 3. Atom numbering for compound (II).

are provided in Tables 1 and 2 respectively. Tables 3 and 4 give the bond lengths and angles for (I) and (II).*

The bond distances in the phenyl rings range from 1·356 (10) to 1·402 (8) Å with an average of 1·382 (9) Å in compound (I) and 1·319 (10) to 1·421 (10) Å with an average of 1·379 (12) Å in compound (II). The e.s.d.'s associated with the phenyl-ring atoms C(13), C(14), C(15), C(16) and C(17) in compound (II) are large arising from the large thermal motion associated with these atoms. The C(1)—C(2) bond distance of 1·538 (7) Å in molecule *A* and 1·549 (7) Å in molecule *B* of compound (I) is comparable, within experimental error, to the value of 1·527 (4) Å in benzoin (Haisa, Kashino & Morimoto, 1980), whereas it is 1·481 (7) Å in molecule (II). The dihedral angle between the two terminal phenyl rings is 81·4 (5) (*A*), 78·5 (5) (*B*) and 83·5 (6)° (II). The molecules *A* and *B* in compound (I) and that in compound (II) are all in the *cisoid* conformation with the torsion angle O(1)—C(1)—C(2)—O(2) being −19·3 (6) (*A*), −27·1 (6) (*B*) and 18·1 (7)° (II). In this conformation the O(1)···O(2) distance is 2·693 (5), 2·719 (5) and 2·679 (5) Å respectively in molecules *A*, *B* and (II).

Since the functional groups —C=O and $-OCH_3$ are in *syn* conformation with respect to each other, one might expect an easy Norrish type II reaction *via* γ-H abstraction from C(3) by the oxygen of the carbonyl chromophore followed by bonding of C(1) to C(3) in the resulting biradical species. Detailed crystallographic analyses of α-cyclohexylacetophenones (Ariel, Ramamurthy, Scheffer & Trotter 1983; Ariel & Trotter, 1985, 1986) yielded information regarding the geometry required for γ-H abstraction by an excited carbonyl chromophore. Similarly crystallographic studies on crowded aromatic nitro compounds (Padmanabhan, Döpp, Venkatesan & Ramamurthy, 1986) have provided information on the preferable geometry for γ-H abstraction by an excited nitro group.

In compounds (I) and (II), the hydrogen H(31) which is attached to the γ-carbon is at a distance from O(1) of 2·81 (6) (*A*), 2·58 (5) (*B*) and 2·87 (3) Å (II). In molecule *B* the O(1)···H(31) distance is well within the suggested upper limit of 2·72 Å for γ-H abstraction by an O atom (Appel, Jiang, Scheffer & Walsh, 1983). The angle $\Delta_0[C(1)=O(1)\cdots H(31)]$ formed between H(31) and the carbonyl group is 78 (1) (*A*), 74 (1) (*B*) and 71 (1)° (II), the ideal value of Δ_0 being 90°.

The angle τ, the degree to which the H being abstracted lies outside the mean plane of the carbonyl group, is 52 (1) (*A*), 61 (1) (*B*) and −55 (1)° (II). Wagner (1976) has pointed out that coplanar (τ ≃ 0°) H abstraction is not a strict requirement for Norrish type II processes of ketones. Examples of such non-coplanar H abstraction have been reported by Ariel *et al.* (1983) and Wagner, Giri, Scaiano, Ward, Gabe & Lee (1985)

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *for non-hydrogen atoms in compound* (I) *with e.s.d.'s in parentheses*

The temperature factor is of the form
$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
*A*O(1)	10022 (5)	2721 (4)	5295 (3)	77 (2)
*A*O(2)	9163 (4)	1662 (3)	3776 (2)	59 (1)
*A*C(1)	11177 (6)	2609 (5)	4725 (3)	49 (2)
*A*C(2)	10877 (6)	2245 (4)	3782 (3)	48 (2)
*A*C(3)	8542 (9)	334 (7)	4167 (6)	80 (3)
*A*C(4)	11453 (5)	3520 (5)	3192 (3)	47 (2)
*A*C(5)	10733 (6)	4575 (5)	3405 (3)	54 (2)
*A*C(6)	11196 (7)	5735 (5)	2873 (4)	62 (2)
*A*C(7)	12441 (8)	5868 (6)	2120 (4)	73 (2)
*A*C(8)	13156 (7)	4817 (6)	1901 (3)	74 (3)
*A*C(9)	12683 (6)	3660 (5)	2433 (3)	62 (2)
*A*C(10)	12904 (6)	2877 (4)	4906 (3)	48 (2)
*A*C(11)	13206 (8)	3362 (6)	5727 (4)	68 (2)
*A*C(12)	14771 (9)	3576 (6)	5944 (5)	78 (3)
*A*C(13)	16043 (9)	3291 (7)	5332 (5)	81 (3)
*A*C(14)	15788 (7)	2811 (6)	4526 (5)	73 (3)
*A*C(15)	14222 (6)	2591 (5)	4303 (4)	60 (2)
*B*O(1)	14681 (4)	1116 (4)	−1205 (3)	71 (2)
*B*O(2)	15643 (4)	−466 (3)	−2524 (2)	57 (1)
*B*C(1)	13571 (6)	411 (5)	−1549 (3)	52 (2)
*B*C(2)	13932 (5)	−750 (5)	−2141 (3)	50 (2)
*B*C(3)	16198 (8)	627 (6)	−3168 (4)	73 (2)
*B*C(4)	13448 (6)	−2041 (5)	−1580 (3)	49 (2)
*B*C(5)	14217 (6)	−2093 (6)	−872 (3)	53 (2)
*B*C(6)	13791 (7)	−3292 (6)	−358 (4)	61 (2)
*B*C(7)	12595 (8)	−4418 (6)	−552 (5)	74 (3)
*B*C(8)	11856 (9)	−4348 (7)	−1262 (5)	88 (3)
*B*C(9)	12250 (8)	−3178 (6)	−1773 (4)	70 (2)
*B*C(10)	11845 (6)	589 (5)	−1342 (3)	51 (2)
*B*C(11)	11528 (7)	1556 (5)	−754 (4)	67 (2)
*B*C(12)	9946 (8)	1752 (6)	−547 (5)	78 (3)
*B*C(13)	8720 (7)	1056 (6)	−984 (4)	73 (3)
*B*C(14)	9001 (7)	89 (7)	−1564 (4)	78 (3)
*B*C(15)	10573 (7)	−141 (6)	−1760 (4)	68 (2)

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *for non-hydrogen atoms of compound* (II) *with e.s.d.'s in parentheses*

The temperature factor is of the form
$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
O(1)	7675 (6)	6878 (3)	858	93 (2)
O(2)	6079 (4)	7978 (3)	2233 (4)	74 (1)
C(1)	8147 (6)	6964 (3)	1914 (6)	54 (2)
C(2)	7517 (6)	7648 (3)	2688 (5)	54 (2)
C(3)	4725 (5)	7491 (4)	2544 (7)	74 (2)
C(4)	4172 (9)	7649 (10)	3828 (9)	181 (7)
C(5)	3458 (8)	7679 (7)	1627 (7)	129 (4)
C(6)	9365 (6)	6403 (3)	2392 (6)	52 (2)
C(7)	9805 (6)	6383 (3)	3644 (5)	58 (2)
C(8)	10913 (9)	5837 (4)	4058 (7)	86 (3)
C(9)	11606 (11)	5292 (5)	3245 (9)	109 (4)
C(10)	11221 (10)	5291 (4)	2036 (8)	93 (3)
C(11)	10120 (8)	5836 (4)	1588 (5)	72 (2)
C(12)	8696 (6)	8376 (3)	2729 (6)	63 (2)
C(13)	9119 (7)	8748 (5)	1692 (8)	97 (3)
C(14)	10202 (12)	9386 (6)	1749 (10)	119 (4)
C(15)	10880 (11)	9651 (5)	2862 (17)	142 (6)
C(16)	10473 (11)	9248 (5)	3951 (12)	113 (4)
C(17)	9390 (8)	8618 (4)	3870 (8)	79 (2)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44654 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and angles* (°) *involving non*-H *atoms in* (I)

*A*O(1)–*A*C(1)	1·212 (7)	*B*O(1)–*B*C(1)	1·217 (6)
*A*O(2)–*A*C(2)	1·408 (6)	*B*O(2)–*B*C(2)	1·406 (6)
*A*O(2)–*A*C(3)	1·420 (8)	*B*O(2)–*B*C(3)	1·426 (7)
*A*C(1)–*A*C(2)	1·538 (6)	*B*C(1)–*B*C(2)	1·549 (7)
*A*C(1)–*A*C(10)	1·485 (7)	*B*C(1)–*B*C(10)	1·493 (7)
*A*C(2)–*A*C(4)	1·516 (6)	*B*C(2)–*B*C(4)	1·510 (7)
*A*C(4)–*A*C(5)	1·387 (7)	*B*C(4)–*B*C(5)	1·374 (7)
*A*C(4)–*A*C(9)	1·389 (7)	*B*C(4)–*B*C(9)	1·388 (8)
*A*C(5)–*A*C(6)	1·378 (7)	*B*C(5)–*B*C(6)	1·399 (8)
*A*C(6)–*A*C(7)	1·390 (9)	*B*C(6)–*B*C(7)	1·381 (9)
*A*C(7)–*A*C(8)	1·384 (9)	*B*C(7)–*B*C(8)	1·364 (11)
*A*C(8)–*A*C(9)	1·375 (7)	*B*C(8)–*B*C(9)	1·375 (9)
*A*C(10)–*A*C(11)	1·388 (8)	*B*C(10)–*B*C(11)	1·377 (7)
*A*C(10)–*A*C(15)	1·402 (7)	*B*C(10)–*B*C(15)	1·388 (8)
*A*C(11)–*A*C(12)	1·381 (10)	*B*C(11)–*B*C(12)	1·382 (9)
*A*C(12)–*A*C(13)	1·381 (11)	*B*C(12)–*B*C(13)	1·367 (9)
*A*C(13)–*A*C(14)	1·356 (10)	*B*C(13)–*B*C(14)	1·361 (9)
*A*C(14)–*A*C(15)	1·385 (8)	*B*C(14)–*B*C(15)	1·388 (9)
*A*C(2)–*A*O(2)–*A*C(3)	113·3 (4)	*B*C(2)–*B*O(2)–*B*C(3)	113·6 (4)
*A*C(1)–*A*C(1)–*A*C(2)	119·7 (4)	*B*O(1)–*B*C(1)–*B*C(2)	119·2 (4)
*A*C(1)–*A*C(1)–*A*C(10)	121·4 (5)	*B*C(1)–*B*C(1)–*B*C(10)	120·3 (5)
*A*C(2)–*A*C(1)–*A*C(10)	118·9 (4)	*B*C(2)–*B*C(1)–*B*C(10)	120·3 (4)
*A*C(2)–*A*C(2)–*A*C(1)	111·4 (4)	*B*O(2)–*B*C(2)–*B*C(1)	111·2 (4)
*A*C(2)–*A*C(2)–*A*C(4)	107·7 (4)	*B*C(2)–*B*C(2)–*B*C(4)	108·4 (4)
*A*C(1)–*A*C(2)–*A*C(4)	109·4 (4)	*B*C(1)–*B*C(2)–*B*C(4)	109·2 (4)
*A*C(2)–*A*C(4)–*A*C(5)	119·8 (4)	*B*C(2)–*B*C(4)–*B*C(5)	119·4 (4)
*A*C(2)–*A*C(4)–*A*C(9)	121·6 (4)	*B*C(2)–*B*C(4)–*B*C(9)	121·1 (5)
*A*C(5)–*A*C(4)–*A*C(9)	118·6 (4)	*B*C(5)–*B*C(4)–*B*C(9)	119·5 (5)
*A*C(4)–*A*C(5)–*A*C(6)	121·4 (5)	*B*C(4)–*B*C(5)–*B*C(6)	119·6 (5)
*A*C(5)–*A*C(6)–*A*C(7)	119·5 (5)	*B*C(5)–*B*C(6)–*B*C(7)	120·5 (6)
*A*C(6)–*A*C(7)–*A*C(8)	119·4 (6)	*B*C(6)–*B*C(7)–*B*C(8)	118·9 (6)
*A*C(7)–*A*C(8) *A*C(9)	120·8 (5)	*B*C(7)–*A*C(8)–*A*C(9)	121·5 (7)
*A*C(4)–*A*C(9)–*A*C(8)	120·4 (5)	*B*C(4)–*B*C(9)–*B*C(8)	119·9 (6)
*A*C(1)–*A*C(10)–*A*C(11)	118·6 (5)	*B*C(1)–*B*C(10)–*B*C(11)	119·1 (5)
*A*C(1)–*A*C(10)–*A*C(15)	122·8 (4)	*B*C(1)–*B*C(10)–*B*C(15)	121·9 (5)
*A*C(11)–*A*C(10)–*A*C(15)	118·5 (5)	*B*C(11)–*B*C(10)–*B*C(15)	118·9 (5)
*A*C(10)–*A*C(11)–*A*C(12)	121·0 (6)	*B*C(10)–*B*C(11)–*B*C(12)	120·7 (5)
*A*C(11)–*A*C(12)–*A*C(13)	118·9 (7)	*B*C(11)–*B*C(12)–*B*C(13)	119·5 (6)
*A*C(12)–*A*C(13)–*A*C(14)	121·5 (7)	*B*C(12)–*B*C(13)–*B*C(14)	120·6 (6)
*A*C(13)–*A*C(14)–*A*C(15)	120·0 (6)	*B*C(13)–*B*C(14)–*B*C(15)	120·2 (6)
*A*C(10)–*A*C(15)–*A*C(14)	120·1 (5)	*B*C(10)–*B*C(15)–*B*C(14)	119·8 (5)

Table 4. *Bond lengths* (Å) *and angles* (°) *involving non*-H *atoms in* (II)

O(1)–C(1)	1·217 (7)	C(7)–C(8)	1·361 (9)
O(2)–C(2)	1·418 (6)	C(8)–C(9)	1·373 (11)
O(2)–C(3)	1·430 (7)	C(9)–C(10)	1·347 (13)
C(1)–C(2)	1·481 (7)	C(10)–C(11)	1·369 (10)
C(1)–C(6)	1·465 (7)	C(12)–C(13)	1·319 (10)
C(2)–C(12)	1·541 (7)	C(12)–C(17)	1·421 (10)
C(3)–C(4)	1·486 (12)	C(13)–C(14)	1·379 (12)
C(3)–C(5)	1·493 (10)	C(14)–C(15)	1·399 (20)
C(6)–C(7)	1·403 (8)	C(15)–C(16)	1·387 (20)
C(6)–C(11)	1·414 (8)	C(16)–C(17)	1·371 (11)
C(2)–O(2)–C(3)	113·7 (4)	C(6)–C(7)–C(8)	121·0 (5)
C(1)–C(1)–C(2)	119·6 (5)	C(7)–C(8)–C(9)	119·8 (7)
C(1)–C(1)–C(6)	119·5 (5)	C(8)–C(9)–C(10)	121·1 (8)
C(2)–C(1)–C(6)	120·9 (5)	C(9)–C(10)–C(11)	120·5 (7)
C(2)–C(2)–C(1)	113·2 (4)	C(6)–C(11)–C(10)	120·4 (6)
C(2)–C(2)–C(12)	106·4 (4)	C(2)–C(12)–C(13)	119·8 (5)
C(1)–C(2)–C(12)	110·3 (4)	C(2)–C(12)–C(17)	120·1 (5)
C(2)–C(3)–C(4)	112·2 (6)	C(13)–C(12)–C(17)	119·9 (6)
C(2)–C(3)–C(5)	108·1 (5)	C(12)–C(13)–C(14)	118·8 (7)
C(4)–C(3)–C(5)	111·0 (7)	C(13)–C(14)–C(15)	122·6 (10)
C(1)–C(6)–C(7)	122·8 (5)	C(14)–C(15)–C(16)	118·9 (11)
C(1)–C(6)–C(11)	120·0 (5)	C(15)–C(16)–C(17)	117·3 (10)
C(7)–C(6)–C(11)	117·2 (5)	C(12)–C(17)–C(16)	122·4 (7)

where the value of τ is in the range 40 to 50°. In molecule *A* in (I) and in (II) the intramolecular distance O(1)···H(31) as noted earlier exceeds the acceptance limit of 2·72 Å. In these cases the τ value lies within the limit so far observed in reactive molecules (Ariel *et al.*, 1983; Wagner *et al.*, 1985; Padmanabhan *et al.*, 1986). In molecule *B*, although the distance O(1)···H(31) is shorter than the van der Waals sum, the value of τ is quite high, 61 (1) compared with 50°.

Another parameter of significance in intramolecular H abstraction is Δ_H, i.e. the angle C(3)–H(31)···O(1), which should ideally be 180°. But the calculated values for Δ_H in both compounds (I) and (II) are much smaller – 107 (4) (*A*), 113 (4) (*B*) and 103 (3)° (II). These are significantly smaller than the value of $\simeq$135° observed in reactive nitro compounds (Padmanabhan *et al.*, 1986). The C(1)···C(3) distances of 2·990 (9), 2·974 (8) and 3·098 (7) Å in molecules *A*, *B* and (II) respectively are smaller than the van der Waals radii, favourable for the combination of the biradicals.

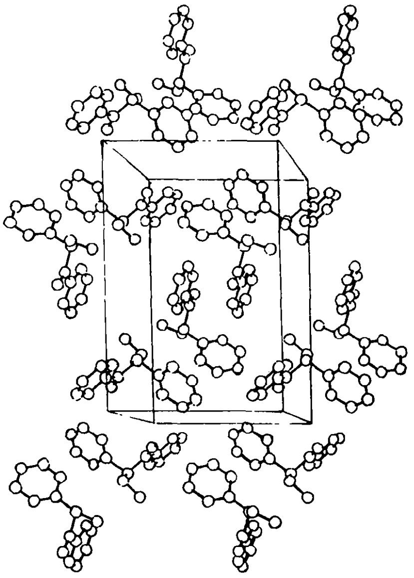

Fig. 4. Packing diagram for (I).

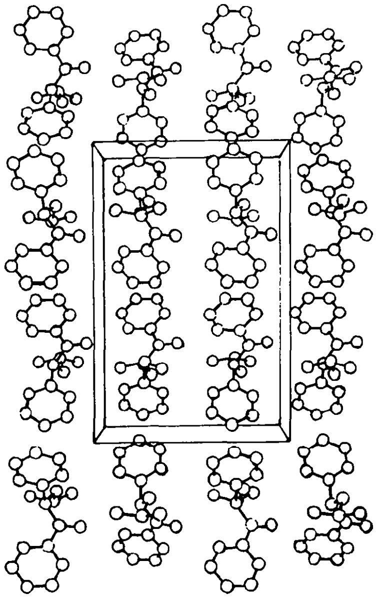

Fig. 5. Packing diagram for (II).

The present crystal structure determination thus suggests that the lack of the photoreaction in the solid state, despite the molecules A, B and (II) all being in the *cisoid* conformation, must be attributed to the overall unfavourable geometrical parameters.

The question at this point is whether the reactivity difference of benzoin alkyl ethers is primarily due to an entirely different conformation of the molecules in the solid benzoin alkyl ethers and in their cyclodextrin complexes. In the absence of detailed X-ray structure analyses of the complex under investigation, the best one could do at this stage is to make some reasonable hypotheses. In the crystals, the molecular motions are very restricted and reactions in the solid state tend to occur with a minimum of atomic and molecular movements (Schmidt, 1971). When molecules of (I) and (II) are complexed with cyclodextrin, the conformation of the molecules may be expected to be in the *cisoid* conformation. It seems reasonable to expect that in the complex the molecular traffic control is not as restrictive as in the crystals of the parent molecule.

The packing diagrams of the molecules (I) and (II) are illustrated in Figs. 4 and 5 respectively. The crystal structures of these molecules are mainly stabilized by van der Waals interactions.

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Structure of 2-Benzimidazolesulfonic Acid Monohydrate

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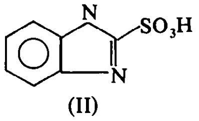
Abstract. $C_7H_6N_2O_3S.H_2O$, $M_r = 216$, monoclinic, $P2_1/n$, $a = 7{\cdot}064\,(2)$, $b = 15{\cdot}507\,(11)$, $c = 9{\cdot}084\,(4)$ Å, $\beta = 110{\cdot}22\,(3)°$, $V = 933{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}54$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}83$ mm^{-1}, $F(000) = 448$, $T = 296$ K, final $R = 0{\cdot}049$ for 1336 unique observed diffractometer data. The mean S—O distance of 1·439 (4) Å is close to the expected value for sulfonic acid structures. Equal bond distances are observed for the three S—O bonds and two C—N bonds indicating complete delocalization of charge over the molecule.

Introduction. 2-Benzimidazolethiol (I) is an important antioxidant used as a corrosion inhibitor, for example with copper (Chadwick & Hoshemi, 1979). Its oxidation products can vary depending on the conditions. The title compound (II) is obtained by using strong oxidants.



(II)

Experimental. Preparation: To 1·5 g (10 mmol) of (I) dissolved in 50 ml methanol, 0·8 g of sodium hydroxide dissolved in 5 ml water was added. To this 25 ml of

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