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Structures and the Photochemical Hydrogen-Abstraction Reaction of Tetraaryl-1,5-pentanediones

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Abstract

The crystal structures of four 1,3,3,5-tetraaryl-1,5-pentanediones have been determined, and correlation of molecular-structure parameters with the photochemical hydrogen-abstraction reaction in the crystalline state is discussed. Crystal data: $T =$ 293 K, Cu $K\alpha$, λ = 1·54184 Å; 1,3,3,5-tetraphenyl-1,5-pentanedione (1*a*), $C_{29}H_{24}O_2$, M_r = 404·51, monoclinic, $C2/c$, a = 18·572 (1), b = 8·4429 (4), c = 15·621 (2) Å, β = 117·554 (6)°, V = 2171·5 (3) Å^3, Z = 4, D_x = 1·238 g cm^{-3}, μ = 5·19 cm^{-1}, $F(000)$ = 856, R = 0·055 for 1444 observed reflections; 9,9-bis(benzoylmethyl)fluorene (1*b*), $C_{29}H_{22}O_2$, M_r = 402·47, tetragonal, $P4_12_12$, a = 12·2109 (6), c = 14·1679 (9) Å, V = 2112·5 (2) Å, Z = 4, D_x = 1·265 g cm^{-3}, μ = 5·33 cm^{-1}, $F(000)$ = 848, R = 0·044 for 956 observed reflections; 1,3,5-triphenyl-3-(4-methylphenyl)-1,5-pentanedione (1*c*) benzene solvate, $C_{30}H_{26}O_2.\frac{1}{2}C_6H_6$, M_r = 457·56, triclinic, $P\bar{1}$, a = 10·084 (1), b = 16·153 (1), c = 8·3716 (8) Å, α = 90·59 (1), β = 112·674 (8), γ = 91·55 (1)°, V = 1257·4 (2) Å^3, Z = 2, D_x = 1·208 g cm^{-3}, μ = 4·97 cm^{-1}, $F(000)$ = 486, R = 0·072 for 3211 observed reflections; 1,3,5-triphenyl-3-(4-bromophenyl)-1,5-pentanedione (1*d*), $C_{29}H_{23}BrO_2$, M_r = 483·37, monoclinic, $P2_1/c$, a = 17·415 (3), b = 8·6254 (9), c = 15·770 (2) Å, β = 98·86 (1)°, V = 2340·5 (6) Å^3, Z = 4, D_x = 1·372 g cm^{-3}, μ = 23·86 cm^{-1}, $F(000)$ = 992, R = 0·061 for 3091 observed reflections. The dibenzoylpropane moieties in the four diketones adopt similar conformations, in which geometrical parameters favor the γ-hydrogen-abstraction process. The relative yields of photoproducts, cyclobutanols and acetophenone, are largely influenced by the structure of the aryl substituents at the 3-position.

Introduction

1,3,3,5-Tetraphenyl-1,5-pentanedione (1*a*) was reported to exhibit photochromism in the solid state (Carvalho, 1935), but the structure of the colored species is still unknown. Our interest in this phenomenon led us to investigate the crystal structures and photochemical behaviour of (1*a*) and some related compounds [(1*b*)–(1*e*)]. Irradiation of compound (1*a*) in the solid state yielded 2-benzoyl-1,3,3-triphenyl-1-cyclobutanol (2*a*), indicating that (1*a*) underwent a Norrish type II reaction, photoinduced γ-hydrogen abstraction and successive cyclization and/or cleavage processes of the carbonyl compounds (see below). Previously it was reported that (1*a*) undergoes a type II reaction in benzene solution, but the product ratio was not fully investigated because of the instability of the cyclization product (2*a*) (Casals, Ferard, Ropert & Keravec, 1975). Type II reactions have been reported for several acetophenone derivatives in the solid state, and favorable conformations discussed for γ-hydrogen abstraction and subsequent cyclization or cleavage processes on the basis of correlation of structural and photochemical data (Evans & Trotter, 1988). In the present paper we report the crystal structures of the diketones (1*a*)–(1*d*) and solid-state photochemical behaviour of (1*a*)–(1*e*). A relationship between the structure and solid-state reactivity of these diketones will be discussed on the basis of molecular parameters. Furthermore, photochemical reactions in solution will be reported in order to compare with those in the solid state.

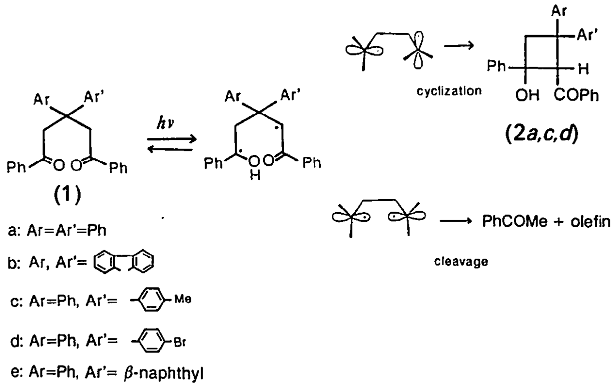

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Table 1. *Data-collection and refinement parameters*

	(1*a*)	(1*b*)	(1*c*)	(1*d*)
Crystal size (mm)	0·4 × 0·25 × 0·2	0·4 × 0·25 × 0·15	0·6 × 0·4 × 0·25	0·3 × 0·25 × 0·15
Reflections for cell parameters				
Number	21	15	18	18
2θ range (°)	43–59	41–54	47–66	53–60
Intensity measurements				
$2\theta_{max}$ (°)	125·0	125·0	125·0	125·0
h	$-18 \rightarrow 18$	$0 \rightarrow 14$	$-12 \rightarrow 12$	$0 \rightarrow 20$
k	$0 \rightarrow 10$	$0 \rightarrow 14$	$-18 \rightarrow 18$	$-10 \rightarrow 0$
l	$0 \rightarrow 17$	$0 \rightarrow 16$	$0 \rightarrow 10$	$-18 \rightarrow 18$
Scan width (°)	0·8 + 0·15tanθ	1·0 + 0·15tanθ	1·0 + 0·15tanθ	1·0 + 0·15tanθ
Unique reflections	1631	1030*	3864	3536
Observed reflections	1444	956	3219†	3097
Structure refinements				
$(\Delta/\sigma)_{max}$	0·04	0·03	0·2‡	0·1
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0·17/−0·27	0·13/−0·20	0·22/−0·27	0·45/−0·58
R	0·055	0·044	0·072	0·061
wR	0·076	0·049	0·082	0·075
$w = [\sigma^2(\lvert F_o \rvert) + a\lvert F_o \rvert^2]^{-1}$				
a value	0·011	0·004	0·004	0·004
S	1·00	1·18	1·26	1·22

* Each pair of equivalent reflections $F_o(hkl)$ and $F_o(khl)$ was averaged.

† Eight reflections (001, $0\bar{1}1$, $1\bar{2}1$, $1\bar{1}1$, $2\bar{1}1$, $\bar{1}\bar{1}2$, 002, 012), which seemed to suffer from extinction, were removed and 3211 reflections were used for structure determination.

‡ For the diketone molecule.

Experimental

The preparation of the diketones (1*a*)–(1*d*) has been reported (Shibuya, Nabeshima, Nagano & Maeda, 1988). (1*e*) was synthesized from acetophenone and 2-benzoylnaphthalene by the method of Carvalho (1935). Colorless plate-like crystals of the compounds were obtained by recrystallization. (1*a*) and (1*b*) were crystallized from benzene–hexane and benzene respectively. The crystals of (1*c*) and (1*d*) obtained from benzene contain solvent of crystallization with a diketone:benzene ratio of 2:1. In the case of (1*d*), however, crystals with suitable dimensions were not obtained, so a crystal obtained from ethanol was used for the X-ray analysis. Intensities were measured at 293 K on a Rigaku AFC-4 diffractometer with graphite-monochromated Cu *Kα* radiation, using the ω–2θ scan technique with a scan speed of 8° min^{-1} in 2θ. Background counts were accumulated for 5 s before and after each scan. Three standard reflections were monitored every 50 reflections and no significant variation in intensity was observed. Lorentz and polarization corrections were made, but no correction was made for absorption.

The structures were determined by direct methods with the program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) for (1*a*) and (1*d*), or *XTAL*2.4 (Hall & Stewart, 1988) for (1*b*) and (1*c*), and refined by full-matrix least-squares methods on *F* with *SHELX*76 (Sheldrick, 1976). Some of the H atoms were located from difference maps while others were assigned geometrically calculated positions and refined. For the diketone (1*c*) the positions of the H atoms in the methyl group were refined as a rigid body in which C—H was taken to be 1·00 Å and H—C—H angles defined as tetrahedral. The final refinements were made with anisotropic and isotropic thermal parameters for the non-H and H atoms respectively. Details of data collection and refinement for (1*a*)–(1*d*) are summarized in Table 1. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Calculations were carried out on a HITAC M-680 computer at the Computer Centre of the University of Tokyo and an IBM 4381-R24 computer at Ochanomizu University.

Solid-state photolyses were carried out in KBr pellets with a 100 W high-pressure mercury lamp. The progress of the reaction was monitored by difference IR spectra and irradiation was continued until the growth of the ν_{O-H} band around 3550 cm^{-1} stopped. The products were analyzed by ^{1}H NMR spectra after the irradiated reaction mixture was extracted in an appropriate deuterated solvent. The photolyses of acetone-d_6 solutions of (1*a*)–(1*e*) were performed with a 400 W xenon lamp at approximately 273 K, monitored by ^{1}H NMR spectra. Difference IR spectra were obtained on a JASCO A302 IR spectrometer connected to a JASCO DP-A330 IR data processor. ^{1}H NMR spectra were recorded on a JEOL JNM-GX270 spectrometer.

Discussion

Final positional parameters for (1*a*)–(1*d*) are listed in Table 2.* The molecular structures, with atomic

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* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, observed and calculated structure factors, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53201 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms*

$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}
(1*a*)				
O(1)	3945 (1)	601 (2)	1492 (1)	5·5
C(2)	4078 (1)	816 (2)	2322 (1)	3·8
C(3)	4526 (1)	2270 (2)	2892 (1)	4·0
C(4)	5000	3295 (3)	2500	3·6
C(5)	3787 (1)	−348 (2)	2805 (1)	3·5
C(6)	3902 (1)	−191 (2)	3749 (1)	4·4
C(7)	3606 (2)	−1326 (3)	4144 (2)	5·4
C(8)	3183 (1)	−2619 (3)	3609 (2)	5·2
C(9)	3070 (2)	−2804 (3)	2678 (2)	5·1
C(10)	3370 (1)	−1673 (2)	2286 (1)	4·2
C(11)	5555 (1)	4379 (2)	3348 (1)	3·7
C(12)	6389 (1)	4305 (2)	3815 (1)	4·2
C(13)	6846 (1)	5332 (3)	4579 (1)	4·8
C(14)	6473 (1)	6427 (2)	4881 (1)	5·1
C(15)	5631 (2)	6498 (3)	4426 (2)	6·3
C(16)	5180 (2)	5493 (3)	3674 (2)	5·6
(1*b*)				
O(1)	4722 (2)	4065 (2)	1147 (2)	6·5
C(2)	4239 (3)	4935 (2)	1099 (2)	4·3
C(3)	4669 (3)	5897 (3)	546 (2)	4·1
C(4)	5765 (2)	5765 (2)	0	3·8
C(5)	3158 (2)	5067 (3)	1598 (2)	4·3
C(6)	2723 (3)	4178 (4)	2071 (3)	5·8
C(7)	1752 (3)	4278 (5)	2566 (3)	7·4
C(8)	1217 (3)	5266 (5)	2600 (3)	7·4
C(9)	1633 (3)	6143 (4)	2123 (3)	7·0
C(10)	2598 (3)	6048 (3)	1620 (3)	5·6
C(11)	6756 (2)	5903 (2)	650 (2)	3·8
C(12)	7097 (3)	5263 (3)	1399 (2)	4·8
C(13)	8030 (3)	5573 (3)	1905 (2)	5·4
C(14)	8600 (3)	6507 (3)	1670 (3)	5·1
C(15)	8278 (2)	7145 (3)	920 (2)	4·5
C(16)	7349 (2)	6834 (2)	408 (2)	3·7
(1*c*)				
O(1)	668 (3)	3047 (1)	1119 (3)	5·8
C(2)	260 (3)	2316 (2)	1071 (4)	4·1
C(3)	664 (3)	1812 (2)	2672 (4)	4·1
C(4)	1947 (3)	2107 (2)	4337 (3)	3·6
C(5)	3221 (3)	2462 (2)	3909 (4)	4·1
C(6)	3655 (3)	1982 (2)	2646 (4)	4·2
O(7)	3215 (3)	1272 (1)	2161 (3)	6·1
C(21)	−707 (3)	1932 (2)	−628 (3)	3·8
C(22)	−1201 (4)	2421 (2)	−2055 (4)	5·1
C(23)	−2111 (4)	2166 (3)	−3645 (5)	6·2
C(24)	−2534 (4)	1285 (3)	−3829 (5)	5·9
C(25)	−2060 (4)	785 (2)	−2438 (5)	5·6
C(26)	−1146 (3)	1094 (2)	−829 (4)	4·6
C(41)	1560 (3)	2808 (2)	5333 (3)	3·5
C(42)	349 (3)	3271 (2)	4670 (4)	3·9
C(43)	78 (3)	3906 (2)	5626 (4)	4·3
C(44)	1019 (3)	4097 (2)	7288 (4)	4·2
C(45)	2231 (4)	3633 (2)	7962 (4)	4·5
C(46)	2503 (4)	3009 (2)	7017 (4)	4·4
C(47)	720 (5)	4764 (2)	8365 (5)	5·9
C(411)	2365 (3)	1361 (2)	5532 (3)	3·8
C(412)	1346 (4)	1039 (2)	6147 (5)	5·1
C(413)	1653 (4)	388 (2)	7262 (5)	5·9
C(414)	2974 (4)	39 (2)	7831 (5)	5·5
C(415)	3985 (4)	342 (2)	7239 (4)	5·0
C(416)	3681 (3)	997 (2)	6105 (4)	4·4
C(61)	4701 (3)	2392 (2)	1989 (3)	3·7
C(62)	5265 (3)	3193 (2)	2494 (4)	4·4
C(63)	6224 (4)	3533 (2)	1832 (4)	5·2
C(64)	6608 (3)	3083 (2)	677 (4)	5·1
C(65)	6043 (3)	2299 (2)	165 (4)	5·0
C(66)	5084 (3)	1949 (2)	816 (4)	4·3
C(101)	6249 (5)	4815 (3)	6269 (6)	6·8
C(102)	4961 (5)	4549 (3)	6342 (7)	6·7
C(103)	3719 (5)	4736 (2)	5072 (6)	6·2
(1*d*)				
Br*	45586 (3)	1627 (7)	39327 (4)	7·6
O(1)	3321 (3)	7065 (4)	2045 (2)	8·1
C(2)	3190 (3)	6866 (5)	1267 (2)	5·2
C(3)	2776 (3)	5446 (5)	877 (3)	5·2
C(4)	2361 (2)	4380 (5)	1448 (3)	4·9
C(5)	1914 (3)	5320 (6)	2045 (3)	5·4
C(6)	1462 (2)	6739 (5)	1690 (2)	4·9
O(7)	1291 (2)	6942 (4)	917 (2)	6·9
C(21)	3467 (2)	8035 (4)	687 (2)	4·8
C(22)	3351 (3)	7868 (6)	−195 (3)	6·0
C(23)	3626 (3)	8992 (8)	−703 (3)	7·0
C(24)	3995 (4)	10262 (8)	−330 (5)	7·5
C(25)	4111 (3)	10454 (7)	547 (4)	6·8
C(26)	3848 (3)	9341 (5)	1053 (3)	5·7
C(41)	2934 (2)	3349 (4)	2042 (2)	4·6
C(42)	3730 (2)	3490 (5)	2137 (3)	5·1
C(43)	4217 (2)	2529 (5)	2692 (3)	5·3
C(44)	3896 (2)	1421 (4)	3152 (2)	5·1
C(45)	3106 (2)	1240 (5)	3080 (3)	6·0
C(46)	2636 (2)	2207 (5)	2530 (3)	5·9
C(411)	1830 (2)	3299 (5)	834 (3)	4·9
C(412)	2186 (3)	2239 (6)	338 (3)	6·7
C(413)	1760 (3)	1217 (7)	−213 (4)	7·8
C(414)	956 (3)	1189 (5)	−301 (3)	6·3
C(415)	600 (3)	2229 (5)	172 (3)	6·1
C(416)	1036 (3)	3253 (5)	731 (3)	5·5
C(61)	1224 (2)	7897 (4)	2297 (2)	4·5
C(62)	868 (3)	9247 (5)	1964 (3)	5·5
C(63)	622 (3)	10343 (6)	2493 (4)	6·7
C(64)	734 (3)	10105 (7)	3369 (4)	6·8
C(65)	1079 (3)	8773 (7)	3714 (3)	6·8
C(66)	1330 (3)	7668 (5)	3186 (3)	5·5

* Coordinates multiplied by 10^5.

numbering, are shown in Fig. 1, and the crystal structures are shown in Fig. 2.

The four diketone molecules adopt similar conformations. (1*a*) and (1*b*) show twofold symmetry and the molecular axis coincides with a crystallographic twofold rotational axis. Molecules (1*c*) and (1*d*) are also nearly symmetrical except for the substitutents at C(44). The benzoyl groups in (1*a*)–(1*d*) are almost planar; each benzoyl group is *gauche* with one aryl group on C(4) and *anti* with the other. However, in each case the torsion angle $C_{C=O}—C_\alpha—C_\beta—C_\gamma$ deviates from 60°, the value expected for a normal staggered arrangement of the $C_\alpha—C_\beta$ bond. This deviation, which is probably a result of steric repulsion between the benzoyl grop and the β-aryl group, causes the γ-H atom to move closer to the carbonyl O atom. In (1*a*), (1*c*) and (1*d*) the two phenyl rings on C(4) are almost perpendicular to each other: the dihedral angles are 83·6 (1), 80·7 (1) and 83·4 (1)°, respectively. On the other hand, the fluorene moiety in (1*b*) is planar with a maximum deviation of 0·03 Å. As is seen in Fig. 1(*b*), the temperature factors of the atoms in the fluorene ring are smaller than those of the phenyl ring C(5)—C(10), indicating that the fluorene moiety in (1*b*) is less flexible than the rest of the molecule. In the phenyl ring C(11)–C(16) of (1*b*), which is part of the fluorene ring, the bond distances (1·375–1·399 Å) (Table 3) correspond to a normal aromatic C—C distance and the bond angles are almost 120° except around C(11) and C(16), which are shared with the five-membered ring. As a result of connecting the two phenyl rings C(11)–C(16) and C(11′)–C(16′), the bond angle C(11)—C(4)—C(11′) in (1*b*) is smaller than in (1*a*), which in turn causes some increase in C(3)—C(4)—C(3′).

The molecular packing differs in the four compounds (1*a*)–(1*d*). In the benzene solvate of (1*c*) the solvent molecule is located at an inversion center, so that each unit cell contains two molecules of (1*c*) and one molecule of benzene (Fig. 2*c*). The included benzene molecule mainly interacts with the aryl groups of two (1*c*) molecules through van der Waals forces. In (1*d*) a short intermolecular Br···Br contact of 3·490 (1) Å was observed between two (1*d*) molecules, which are related by an inversion center. There were no other unusually short contacts in all four compounds. In spite of the differences in molecular packing, the four diketone molecules adopt a very similar conformation as described above, suggesting that intermolecular forces have only a small effect on the molecular structure in this system.

It is well known that the structural requirements for γ-H abstraction by the (n,π^*) excited carbonyl oxygen can be expressed with the three geometrical parameters, which are depicted in Fig. 3. Δ is defined as the angle between the carbonyl C, carbonyl O and the γ-H atoms ($\angle$C=O···H), and τ as the angle between the O—H vector and the carbonyl plane. The ideal geometry for the type II process is for the H atom to be abstracted to be located in the direction of the n orbital on the carbonyl O with a distance shorter than sum of van der Waals radii, that is, O···H < 2·72 Å, $\Delta = 90°$ and $\tau = 0°$. However, as has been pointed out, coplanar hydrogen abstraction is not a strict requirement for the type II process, and the carbonyl systems with a certain amount of deviation ($\tau \simeq 30$–$50°$) from coplanar geometry effectively undergo the γ-H abstraction reaction in the solid state (Ramamurthy & Venkatesan, 1987). The values of the three parameters for (1*a*)–(1*d*) are listed in Table 4. In all the diketones each carbonyl group has a γ-H atom suitably oriented for abstraction. The O···H distance is less than 2·72 Å, Δ (100·3–107·4°) is close to the ideal value of 90°, and τ (15·6–36·8°) deviates from 0° to some extent, but the deviation seems to be tolerated for the type II process. The two carbonyl groups in (1*c*) or (1*d*), which are non-equivalent in the crystals, have closely similar hydrogen-abstraction parameters, and therefore, they are expected to show comparable photoreactivity.

As shown in Table 5, the photoreactivity of the carbonyl group in the diketones (1*a*)–(1*d*) was considerably affected by the aryl substituents at C(4). Diketones (1*a*), (1*c*) and (1*d*) showed relatively high reactivity, and (1*a*) and (1*c*) gave cyclobutanols (2*a*) and (2*c*) respectively as almost the only product. On photolysis of (1*d*) the corresponding cyclobutanol

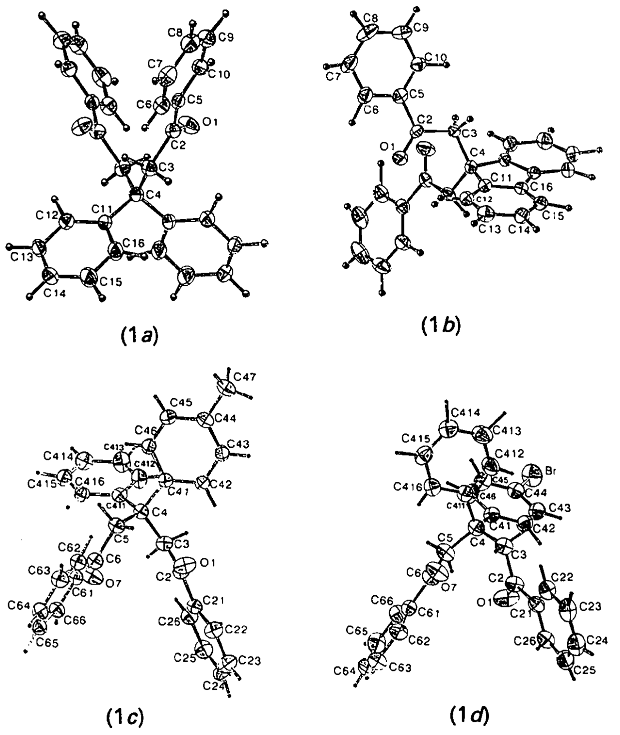

Fig. 1. *ORTEP* plots of (1*a*)–(1*d*) with atomic numbering. The anisotropic ellipsoids for non-H atoms enclose 30% probability.

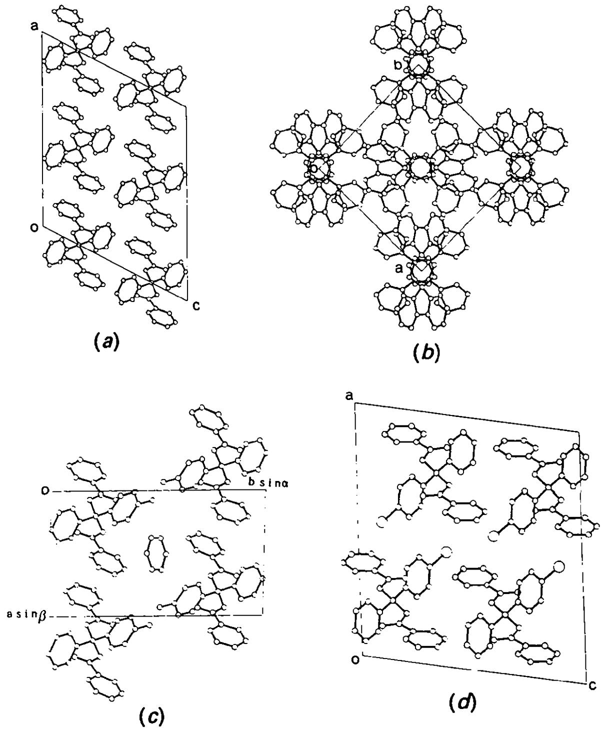

Fig. 2. Crystal structures of (1*a*)–(1*d*): (*a*) viewed along the *b* axis, (*b*) viewed along the *c* axis, (*c*) viewed along the *c* axis, (*d*) viewed along the *b* axis.

Table 3. *Selected bond distances* (Å) *and angles* (°)

(1*a*)			
O(1)—C(2)	1·217 (3)	C(3)—C(4)	1·548 (3)
C(2)—C(3)	1·519 (3)	C(4)—C(11)	1·547 (3)
C(2)—C(5)	1·484 (3)		
O(1)—C(2)—C(3)	122·1 (2)	C(3)—C(4)—C(3′)	112·0 (2)
O(1)—C(2)—C(5)	120·1 (2)	C(3)—C(4)—C(11)	105·5 (2)
C(3)—C(2)—C(5)	117·9 (2)	C(3)—C(4)—C(11′)	113·2 (2)
C(2)—C(3)—C(4)	118·5 (2)	C(11)—C(4)—C(11′)	107·5 (2)
(1*b*)			
O(1)—C(2)	1·218 (4)	C(11)—C(16)	1·390 (4)
C(2)—C(3)	1·506 (4)	C(12)—C(13)	1·398 (5)
C(2)—C(5)	1·506 (4)	C(13)—C(14)	1·377 (5)
C(3)—C(4)	1·554 (4)	C(14)—C(15)	1·375 (5)
C(4)—C(11)	1·530 (4)	C(15)—C(16)	1·399 (4)
C(11)—C(12)	1·383 (4)	C(16)—C(16′)	1·459 (4)
O(1)—C(2)—C(3)	122·8 (3)	C(4)—C(11)—C(16)	110·7 (2)
O(1)—C(2)—C(5)	119·4 (3)	C(12)—C(11)—C(16)	119·7 (3)
C(3)—C(2)—C(5)	117·9 (3)	C(11)—C(12)—C(13)	119·1 (3)
C(2)—C(3)—C(4)	118·6 (3)	C(12)—C(13)—C(14)	120·8 (4)
C(3)—C(4)—C(3′)	115·3 (2)	C(13)—C(14)—C(15)	120·8 (3)
C(3)—C(4)—C(11)	111·7 (2)	C(14)—C(15)—C(16)	118·6 (3)
C(3)—C(4)—C(11′)	108·2 (2)	C(11)—C(16)—C(15)	121·1 (3)
C(11)—C(4)—C(11′)	100·8 (2)	C(11)—C(16)—C(16′)	108·9 (2)
C(4)—C(11)—C(12)	129·6 (3)	C(15)—C(16)—C(16′)	130·0 (3)
(1*c*)			
O(1)—C(2)	1·235 (4)	C(4)—C(411)	1·535 (4)
C(2)—C(3)	1·498 (5)	C(5)—C(6)	1·506 (5)
C(2)—C(21)	1·496 (4)	C(6)—O(7)	1·226 (4)
C(3)—C(4)	1·552 (4)	C(6)—C(61)	1·508 (4)
C(4)—C(5)	1·558 (4)	C(44)—C(47)	1·507 (6)
C(4)—C(41)	1·544 (4)		
O(1)—C(2)—C(3)	121·9 (3)	C(5)—C(4)—C(41)	105·8 (2)
O(1)—C(2)—C(21)	118·9 (3)	C(5)—C(4)—C(411)	112·6 (2)
C(3)—C(2)—C(21)	119·1 (3)	C(41)—C(4)—C(411)	107·3 (2)
C(2)—C(3)—C(4)	119·6 (3)	C(4)—C(5)—C(6)	118·1 (3)
C(3)—C(4)—C(5)	111·4 (2)	C(5)—C(6)—O(7)	122·8 (3)
C(3)—C(4)—C(41)	113·0 (2)	C(5)—C(6)—C(61)	118·2 (3)
C(3)—C(4)—C(411)	106·8 (2)	O(7)—C(6)—C(61)	119·1 (3)
(1*d*)			
O(1)—C(2)	1·226 (6)	C(4)—C(411)	1·545 (6)
C(2)—C(3)	1·504 (7)	C(5)—C(6)	1·514 (7)
C(2)—C(21)	1·490 (6)	C(6)—O(7)	1·223 (5)
C(3)—C(4)	1·542 (6)	C(6)—C(61)	1·486 (6)
C(4)—C(5)	1·542 (7)	C(44)—Br	1·894 (4)
C(4)—C(41)	1·541 (6)		
O(1)—C(2)—C(3)	121·8 (4)	C(5)—C(4)—C(41)	105·8 (4)
O(1)—C(2)—C(21)	119·4 (4)	C(5)—C(4)—C(411)	113·0 (4)
C(3)—C(2)—C(21)	118·7 (4)	C(41)—C(4)—C(411)	107·5 (3)
C(2)—C(3)—C(4)	119·0 (4)	C(4)—C(5)—C(6)	118·8 (4)
C(3)—C(4)—C(5)	111·7 (4)	C(5)—C(6)—O(7)	121·2 (4)
C(3)—C(4)—C(41)	112·4 (3)	C(5)—C(6)—C(61)	119·0 (4)
C(3)—C(4)—C(411)	106·4 (3)	O(7)—C(6)—C(61)	119·8 (4)

(2*d*) was formed as the main product. For these three diketones cyclization of the biradical intermediate occurred preferentially to give a high (cyclization/cleavage) ratio in the solid state. A possible explanation for the high selectivity of cyclobutanol in the solid-state reactions of (1*a*), (1*c*) and (1*d*) is as follows: the 1,4-biradical formed by γ-H abstraction can potentially take one of three reaction pathways, that is, cyclization, cleavage, and reverse hydrogen transfer leading to the starting ketone. For the geometry of the biradical involved with the Norrish type II reaction it has been suggested that cleavage can occur most effectively when the two radical *p* orbitals are parallel to the C_α—C_β bond being broken, while large deviations from the parallel alignment appear to favor cyclization as shown in the scheme (Evans & Trotter, 1988). Assuming that a radical *p* orbital on the carbonyl C atom is perpendicular to the carbonyl plane, in all the four molecules investigated this orbital forms an angle greater than 70° with the C_α—C_β bond, and so large rotational motions will be required to achieve a suitable conformation for cleavage. It is likely that restriction of such motions in the solid state would favor cyclization over cleavage.

In contrast to (1*a*), (1*c*) and (1*d*), both (1*b*) and (1*e*) did not react to give the corresponding cyclobutanols under similar conditions to those of (1*a*), (1*c*) or (1*d*). As shown in Table 4, (1*b*) adopts a similar conformation to that of (1*a*), (1*c*) or (1*d*), and one of the γ-H atoms is suitably located for abstraction by the carbonyl atom. The molecular structure of (1*e*) is probably similar to that of the other four diketons, based on the fact that aryl substituents at C(4) in (1*a*)–(1*d*) have only small effects on the conformation of the dibenzoylpropane moiety. Thus, the low reactivity of (1*b*) and (1*e*) in the solid state cannot be explained only in terms of molecular structure.

Photolyses of the diketones (1*a*)–(1*e*) in acetone were also carried out and the reaction products are shown in Table 5. It appears that in solution β-cleavage processes of the 1,4-biradical intermediates result in a higher ratio of fragmentation to cyclization by the ease of the rotational motion around the C_α—C_β bond than in the solid state. The photoreactivity of (1*b*) and (1*e*) was much lower than that of (1*a*) or (1*c*) even in solution.

In the UV region of the electronic spectra of (1*b*) and (1*e*), the intense absorption band due to a π,π^* transition of the fluorene (λ_{S_1} = 301 nm) or naphthalene (λ_{S_1} = 311 nm) moiety extends up to about 350 nm and overlaps with a much weaker absorption band due to an n,π^* transition of the benzoyl group ($\lambda_{\max}$ = 325 nm; Murov, 1973). As a result, under our experimental conditions, light was absorbed not only by the benzoyl group but also by the aryl chromophore. Previously it was reported that aryl substituents at the β-position can effectively deactivate the carbonyl $^3(n,\pi^*)$ state (Netto-Ferreira, Leigh & Scaiano, 1985). Diketones (1*b*) and (1*e*) have an aryl substituent whose π,π^* triplet energy is lower than that of the benzoyl group $^3(n,\pi^*)$ at the β-position. It is suggested that in the cases of (1*b*) and (1*e*) intramolecular triplet energy transfer will

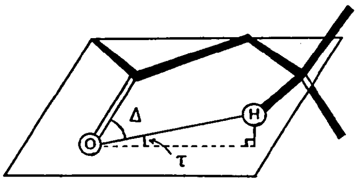

Fig. 3. Definition of hydrogen-abstraction parameters.

Table 4. *Some torsion angles and hydrogen-abstraction parameters*

	(1*a*)	(1*b*)	(1*c*)		(1*d*)		Ideal value*
Torsion angles (°)							
$C_{C=O}—C_\alpha—C_\beta—C_\gamma$	42·0 (3)	43·1 (4)	40·3 (4)	45·4 (4)	42·3 (6)	41·2 (6)	
$O—C_{C=O}—C_\alpha—C_\beta$	14·6 (3)	1·2 (5)	17·7 (5)	12·0 (5)	12·6 (7)	17·7 (7)	
Hydrogen-abstraction parameters							
O···H (Å)	2·37 (3)	2·43 (4)	2·38 (3)	2·39 (3)	2·36 (5)	2·35 (6)	< 2·72
Δ (°)	103·0 (7)	107·4 (10)	100·3 (8)	100·4 (8)	101·9 (12)	100·4 (14)	90
τ (°)	28·8 (7)	15·6 (9)	30·7 (7)	27·9 (8)	30·4 (12)	36·8 (14)	0

* Evans & Trotter (1988).

Table 5. *Yields of photoproducts in the solid state and in solution*

		Solid state			Acetone-d_6	
	Irradiation time (h)	Conversion (%)	(2):acetophenone	Irradiation time (h)	Conversion (%)	(2):acetophenone
(1*a*)	2	29	100:0	22	45	89:11
(1*b*)	2	0		26	3	100:0
(1*c*†)	2	26	100*:0	33	42	92*:8
(1*d*†)	1	15	92*:8	24	8	0:100
(1*e*)	3	0		35	3	0:100

* Total of two diastereomers.
† Benzene solvate.

occur from the benzoyl group to the fluorene or naphthalene moiety and the n,π^* carbonyl triplet of these diketones, *i.e.* the reaction state for a type II reaction will be quenched much more efficiently than that of (1*a*), (1*c*) or (1*d*). This assumption is supported partially by the phosphorescence spectrum of (1*e*) at 77 K, which resembles that of naphthalene rather than acetophenone (Murov, 1973). In the case of the solid-state photolysis of (1*b*), however, it cannot be ruled out that the 1,4-biradical intermediate undergoes exclusively the reverse H-transfer to give the starting diketone. The corresponding cyclobutanol, from (1*b*), would be rather unstable because of the large strain around the spiro C atom in addition to thermal instability of the aldol structure.

With respect to the stereochemistry of (2*a*) there are two possible diastereomers: one in which the OH group is *cis* to the benzoyl group and the other in which the two groups are *trans* to each other. The NMR spectrum showed that one isomer was formed exclusively and the product was identical both in the solid state and in solution. Although it seems difficult to determine unambiguously which isomer was actually obtained, the IR absorption band at *ca* 3550 cm^{-1} assignable to the O—H stretching band in dilute $CDCl_3$ solution suggests the existence of an intramolecular hydrogen bond, and so (2*a*) can be tentatively assigned as the *cis* isomer. This isomer can be thought of as being much more stable than the *trans* isomer, taking into account the intramolecular hydrogen bonding and lower bulkiness of the OH group compared with the phenyl group. Therefore, exclusive formation of the *cis* isomer both in solution and in the solid state is probably attributable to the relative stability compared with the *trans* isomer. In the cases of (2*c*) and (2*d*) two of four possible isomers were formed with ratio of about 1:1. These two isomers probably differ in the stereochemistry about the C atom which has two aryl groups. This result is considered to reflect almost the same reactivity of the two non-equivalent carbonyl groups in the crystals of (1*c*) or (1*d*), as expected on the basis of the X-ray analysis.

In conclusion, the four diketones (1*a*)–(1*d*) adopt a similar conformation, with each carbonyl group close to a γ-H atom which is suitably oriented for the abstraction reaction. In spite of the similarity of the molecular structure the photoreactivity of these diketones is mainly controlled by the structure of the β-aryl groups. The low reactivity of (1*b*) and (1*e*) suggests that intramolecular energy transfer can effectively occur from the $^3(n,\pi^*)$ state of the benzoyl moiety to the fluorenyl or naphthyl group. In the case of (1*a*), (1*c*) and (1*d*), which showed relatively high reactivity both in acetone solution and in the solid state, the higher (cyclization/cleavage) ratio in the solid state can be explained in terms of the restriction of the rotational motion around the $C_\alpha—C_\beta$ bond of the 1,4-biradical intermediate.

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References

Carvalho, A. P. (1935). *Ann. Chim. (Paris)*, **4**, 449–522.

Casals, P.-F., Ferard, J., Ropert, R. & Keravec, M. (1975). *Tetrahedron Lett.* pp. 3909–3912.

Evans, S. V. & Trotter, J. (1988). *Acta Cryst.* B**44**, 63–72.

Hall, S. R. & Stewart, J. M. (1988). Editors. *XTAL*2.4 *User's Manual*. Univs. of Western Australia, Australia and Maryland, USA.

International Tables of X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Murov, S. L. (1973). Editor. *Handbook of Photochemistry*. New York: Marcel Dekker.
Netto-Ferreira, J. C., Leigh, W. J. & Scaiano, J. C. (1985). *J. Am. Chem. Soc.* **107**, 2617–2622.
Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Shibuya, J., Nabeshima, M., Nagano, H. & Maeda, K. (1988). *J. Chem. Soc. Perkin Trans. 2*, pp. 1607–1612.

Acta Cryst. (1990). **B46**, 671–675

Dynamic Conformational Behaviour of an Eleven-Membered Ring in the Solid State. X-ray Studies of Cycloundecylmethyl 1-Naphthylcarbamate at 120 and 293 K

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Abstract

The crystal structure of cycloundecylmethyl 1-naphthylcarbamate is ordered at 120 K and the eleven-membered ring exhibits the [12323] conformation of cycloundecane with C—C(sp^3)—C angles enlarged beyond tetrahedral, 112·1–118·4 (3)°. The crystal structure is disordered at 293 K in the region occupied by the eleven-membered ring and molecular-mechanics calculations establish that the major component of the conformational mixture has the [335] cycloundecane conformation. X-ray studies at 293 K before and after cooling a crystal to 120 K for *ca* 120 h confirmed that the order–disorder transformation is reversible. The [12323]$\rightleftarrows$[335] conformational interconversion has been detected previously for cycloundecane in solution. $C_{23}H_{31}NO_2$, $M_r = 353{\cdot}54$, monoclinic, $P2_1/c$, $Z = 4$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $F(000) = 768$. At 293 K, $a = 8{\cdot}789\ (3)$, $b = 26{\cdot}393\ (4)$, $c = 9{\cdot}237\ (2)$ Å, $\beta = 107{\cdot}33\ (2)°$, $V = 2045\ (1)$ Å^3, $D_x = 1{\cdot}15$ Mg m^{-3}, $\mu = 0{\cdot}57$ mm^{-1}, $R = 0{\cdot}079$ for 2288 independent reflections with $I > 2{\cdot}5\sigma(I)$; $a = 8{\cdot}792\ (2)$, $b = 26{\cdot}394\ (3)$, $c = 9{\cdot}239\ (1)$ Å, $\beta = 107{\cdot}35\ (2)°$, $V = 2046\ (1)$ Å^3, $R = 0{\cdot}073$ for 2185 reflections with $I > 2{\cdot}5\sigma(I)$. At 120 K, $a = 8{\cdot}568\ (3)$, $b = 26{\cdot}227\ (5)$, $c = 9{\cdot}183\ (2)$ Å, $\beta = 107{\cdot}91\ (2)°$, $V = 1964\ (1)$ Å^3, $D_x = 1{\cdot}20$ Mg m^{-3}, $\mu = 0{\cdot}59$ mm^{-1}, $R = 0{\cdot}049$ for 3055 independent reflections with $I > 2{\cdot}5\sigma(I)$.

Introduction

Equilibria involving conformational interconversions of organic molecules in liquids have been extensively studied (Eliel, Allinger, Angyal & Morrison, 1965; Riddell, 1980; Berg & Sandström, 1986, 1987) but few analogous transformations in solids have been recognized, though a variety of other processes involving atomic and molecular displacements in crystals are known (Gavezzotti & Simonetta, 1987; Bernstein, 1987). A dynamic equilibrium between two or more conformers in a single crystal will result in a disordered crystal structure and the population of various conformers at the disordered site will vary with temperature in accord with the Boltzmann distribution. X-ray structural analyses at several temperatures have characterized chair$\rightleftarrows$boat interconversion of six-membered rings in some derivatives of bicyclo[3.3.1]nonan-9-one (G. A. Sim, unpublished results) and axial$\rightleftarrows$equatorial interchange at the N atoms in 1,3,5-tribenzyl-1,3,5-triazacyclohexane (Sim, 1987). Cycloundecane undergoes facile conformational exchange in solution at low temperatures (Anet, Cheng & Wagner, 1972) and this prompted us to investigate compounds incorporating eleven-membered rings.

Force-field calculations for cycloundecane have identified six conformations within an energy span of 11 kJ mol^{-1}, with the two lowest-energy conformations, [335] and [12323], being nearly identical in strain energy (Anet & Rawdah, 1978). The NMR spectra of cycloundecane demonstrate conformational exchange in solution down to *ca* 120 K and this has been interpreted in terms of interconversion of the [335] and [12323] forms and pseudorotation of the former (Anet & Rawdah, 1978). Conformational data for simple derivatives of cycloundecane in the solid state are sparse; X-ray results for cycloundeca-

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