

Crystal Structure and Photochemistry of α -Adamantylacetophenone* and Two Polymorphs of α -Adamantyl-*p*-chloroacetophenone†

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Abstract

The photochemical fragmentation reactions of adamantylacetophenones have been studied by crystal structure analyses of three derivatives and by correlation of the crystal and molecular structure parameters with photochemical behaviour. Crystal data are: $T = 295$ K, Mo $K\alpha_1$, $\lambda = 0.70930$ Å; α -1-adamantylacetophenone, $C_{18}H_{22}O$, $M_r = 254.37$, $Pca2_1$, $a = 11.7741$ (13), $b = 10.6162$ (9), $c = 11.3257$ (13) Å, $Z = 4$, $R = 0.032$ for 873 reflections with $I \geq 3\sigma(I)$; α -1-adamantyl-4-chloroacetophenone, $C_{18}H_{21}ClO$, $M_r = 288.82$; form *a*, $C2/c$, $a = 40.603$ (9), $b = 6.5671$ (8), $c = 11.814$ (3) Å, $\beta = 102.053$ (11)°, $Z = 8$, $R = 0.042$ for 1494 reflections; form *b*, $P2_1/n$, $a = 17.352$ (4), $b = 6.5950$ (8), $c = 13.038$ (3) Å, $\beta = 90.956$ (8)°, $Z = 4$, $R = 0.039$ for 1587 reflections. The molecules all have similar conformations, which differ from those of related cycloalkyl analogues; the principal differences between the *p*-chloro derivative molecules in the two crystal forms are 20° in one torsion angle and 40° in the orientation of the aromatic rings. Each molecule has a γ -H atom favourably sited for abstraction by oxygen in a photochemical reaction, and the nature and amount of photoproducts can be rationalized on the basis of this reaction mechanism.

Introduction

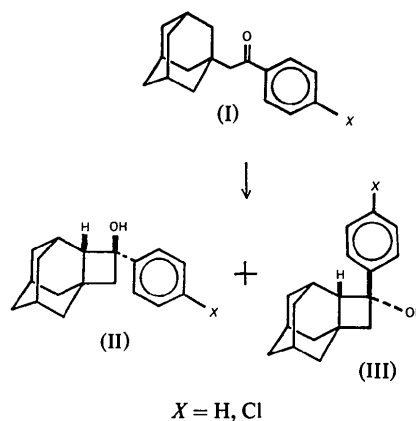
Structural and photochemical studies of substituted acetophenones (Evans & Trotter, 1988*a,b*) have now been extended to α -adamantyl derivatives (I). These compounds were chosen since they contain a conformationally rigid ring system, which further restricts the possible motions of the molecules in solution and in the solid state. In addition, the photoreactions are considerably simplified for two reasons:

(i) Cleavage of the adamantylacetophenone radicals is not possible, since this would produce an impossibly strained adamantene, with a double bond at a bridge-head C atom (Sauers, Gorodetsky, Whittle & Hu, 1971; Lewis, Johnson & Kory, 1974; Gagosian, Dalton

& Turro, 1975) and only cyclization products are formed.

(ii) In the cyclization products, there is no ambiguity regarding the *cis* or *trans* configuration of the junction between the four- and six-membered rings, since the junction is *cis* with respect to one of the six-membered rings of the adamantane skeleton and *trans* with respect to the neighbouring six-membered ring.

Hence, the only possible photoproducts are the two cyclobutanols [(II) and (III)], with *cis*- or *trans*-OH substituents (relative to the ring-junction H atom). The present paper describes the crystal structures and photochemistry of α -1-adamantylacetophenone (H-Ad) and α -1-adamantyl-*p*-chloroacetophenone (Cl-Ad); the *p*-chloro compound is found in two crystal forms, which have somewhat different molecular conformations and solid-state photochemical behaviour.



Experimental

Data, measured with a Nonius CAD-4F diffractometer by the usual techniques (Evans & Trotter, 1988*a*), are summarized in Table 1. The structures were determined by direct methods and refined by full-matrix least-squares procedures, with $w = 1/\sigma^2(F)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04I)^2$, S = scan, B_1 and B_2 = background counts. Scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard

* 1-Phenyl-2-tricyclo[3.3.1.1^{3,7}]dec-1-ylethanone.

† 1-(4-Chlorophenyl)-2-tricyclo[3.3.1.1^{3,7}]dec-1-ylethanone.

Table 1. *Crystal data, data collection and refinement parameters*

Compound Formula <i>M_r</i>	H-Ad C ₁₈ H ₂₂ O 254.37		Cl-Ad C ₁₈ H ₂₁ ClO 288.82	
	Prism		Plate (form <i>a</i>)*	Needle (form <i>b</i>)*
Crystal habit	Prism		Plate (form <i>a</i>)*	Needle (form <i>b</i>)*
Dimensions (mm) (cut fragments)	0.23 × 0.35 × 0.25		0.35 × 0.35 × 0.35	0.40 × 0.07 × 0.10
Crystal system	Orthorhombic	Monoclinic	Monoclinic	
Space group	<i>Pca</i> 2 ₁	<i>C2/c</i>	<i>P2₁/n</i>	
<i>a</i> (Å)	11.7741 (13)	40.603 (9)	17.352 (4)	
<i>b</i> (Å)	10.6162 (9)	6.5671 (8)	6.5950 (8)	
<i>c</i> (Å)	11.3257 (13)	11.814 (3)	13.038 (3)	
β (°)	—	102.053 (11)	90.956 (8)	
<i>V</i> (Å ³)	1415.7 (3)	3080.7 (11)	1491.8 (6)	
<i>Z</i>	4	8	4	
<i>D_x</i> (g cm ⁻³)	1.193	1.245	1.286	
<i>F</i> (000)	552	1232	616	
μ (Mo) (cm ⁻¹)	0.7	2.4	2.5	
No. of reflections for cell parameter determination	25	20	23	
θ range (°)	12–18	15–18	12–18	
Intensity measurements				
θ_{\max} (°)	25.0	27.5	27.5	
ω scan, <i>a</i>	0.70	0.95	0.80	
(<i>a</i> + <i>b</i> tan θ) ² <i>b</i>	0.35	0.35	0.35	
Scan speeds (° min ⁻¹)	1.1–10	1.5–10	1.3–10	
<i>h</i>	0–13	0–51	–22–22	
<i>k</i>	0–12	0–8	0–8	
<i>l</i>	0–13	–15–14	0–16	
Total unique reflections	1309	3531	3408	
Reflections with <i>I</i> > 3 σ (<i>I</i>)	873	1494	1587	
%	66.7	42.3	46.6	
Structure refinements				
No. of parameters†	172	181 (265)	181 (265)	
Data/parameter ratio†	5.1	8.3 (5.6)	8.8 (6.0)	
Δ/σ mean	0.014	0.005	0.001	
maximum	0.066	0.048	0.005	
$\Delta\rho$ (e Å ⁻³)	±0.11	±0.20	±0.21	
<i>R</i> [<i>I</i> ≥ 3 σ (<i>I</i>)]	0.032	0.042	0.039	
<i>wR</i>	0.035	0.051	0.042	
<i>S</i>	1.86	1.16	1.47	
<i>R</i> (all data)	0.063	0.129	0.122	

* Form *a* crystallized from aqueous ethanol, form *b* from hexane.

† Numbers in brackets include refined H-atom parameters.

Table 2. *Final positional (fractional × 10ⁿ) and equivalent isotropic thermal parameters (Å² × 10³), with standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> *
H-Ad (× 10 ⁴)				
O(1)	598 (2)	3533 (2)	–592 (4)	85
C(1)	1780 (2)	5085 (3)	–1411 (3)	45
C(2)	2793 (2)	5770 (3)	–1393 (4)	55
C(3)	2993 (3)	6696 (3)	–2217 (5)	69
C(4)	2198 (4)	6965 (3)	–3053 (4)	74
C(5)	1186 (3)	6311 (3)	–3082 (4)	63
C(6)	974 (2)	5379 (3)	–2272 (4)	52
C(7)	1519 (3)	4058 (3)	–548 (4)	54
C(8)	2387 (3)	3657 (3)	346 (3)	56
C(9)	3095 (2)	2485 (3)	0	41
C(10)	2388 (3)	1282 (3)	121 (3)	54
C(11)	3116 (2)	123 (3)	–177 (4)	58
C(12)	4125 (3)	37 (3)	656 (3)	61
C(13)	4846 (2)	1222 (3)	517 (4)	57
C(14)	5259 (2)	1335 (3)	–752 (4)	60
C(15)	4242 (3)	1408 (3)	–1582 (4)	53
C(16)	3529 (2)	2560 (3)	–1267 (3)	45
C(17)	4134 (3)	2385 (3)	833 (3)	57
C(18)	3531 (3)	234 (3)	–1443 (4)	63
Cl-Ad- <i>a</i> (× 10 ⁵)				
C(1)	32441 (4)	36568 (28)	53155 (13)	55
C(2)	32416 (5)	32339 (34)	41672 (14)	62
C(3)	30559 (5)	16476 (34)	36080 (16)	65
C(4)	28598 (4)	5161 (30)	41806 (15)	64
C(5)	28532 (5)	9225 (36)	53229 (17)	71
C(6)	30482 (5)	24558 (36)	58783 (16)	70
C(7)	34468 (4)	53315 (38)	59524 (16)	75
C(8)	35651 (5)	70863 (38)	53261 (21)	72
C(9)	39469 (4)	72389 (23)	53744 (12)	48
C(10)	41452 (5)	75769 (36)	66100 (15)	59
C(11)	45175 (5)	78114 (29)	66221 (16)	61
C(12)	45769 (6)	96219 (36)	58801 (19)	74
C(13)	43834 (6)	92631 (34)	46457 (18)	78
C(14)	45133 (7)	73389 (37)	41733 (20)	82
C(15)	44556 (4)	55518 (32)	49223 (16)	64
C(16)	40816 (5)	53256 (30)	48980 (18)	53
C(17)	40113 (6)	90443 (34)	46347 (22)	75
C(18)	46470 (5)	58869 (34)	61493 (19)	68
Cl	26179 (2)	–14299 (10)	34633 (5)	107
O(1)	35127 (4)	52879 (35)	70084 (12)	132
Cl-Ad- <i>b</i> (× 10 ⁴ , Cl × 10 ⁵)				
C(1)	1845 (1)	–1860 (3)	4598 (2)	41
C(2)	1709 (1)	170 (4)	4372 (2)	47
C(3)	2240 (2)	1328 (4)	3865 (2)	51
C(4)	2931 (1)	474 (4)	3613 (2)	50
C(5)	3094 (2)	–1527 (5)	3830 (2)	59
C(6)	2552 (2)	–2666 (4)	4312 (2)	53
C(7)	1271 (1)	–3215 (4)	5085 (2)	49
C(8)	617 (1)	–2364 (5)	5694 (2)	48
C(9)	795 (1)	–2037 (3)	6844 (2)	36
C(10)	1097 (2)	–3978 (4)	7357 (2)	48
C(11)	1232 (2)	–3626 (4)	8505 (2)	54
C(12)	476 (2)	–3032 (4)	9004 (2)	59
C(13)	180 (1)	–1080 (4)	8511 (2)	50
C(14)	767 (2)	608 (4)	8673 (2)	51
C(15)	1519 (1)	–2 (4)	8168 (2)	46
C(16)	1389 (1)	–336 (4)	7025 (2)	42
C(17)	46 (1)	–1408 (5)	7369 (2)	47
C(18)	1821 (2)	–1952 (4)	8663 (2)	55
Cl	36238 (4)	19600 (13)	30139 (6)	81
O(1)	1338 (1)	–5045 (3)	4994 (2)	79

* $U_{eq} = \frac{1}{3} \times \text{trace of diagonalized } U \text{ tensor.}$

computer programs (Evans & Trotter, 1988*a*). Details of the refinements are in Table 1.

Discussion

Final positional parameters are in Table 2 and other data have been deposited.* The molecules (Fig. 1) each contain an adamantyl group with normal bond lengths and angles; for the three structures, C–C = 1.510–1.549 (2–5), mean 1.526 Å, C–C–C angles = 107.8–112.1 (2–3), mean 109.6°. The aromatic rings show some deviations from exact planarity ($\chi^2 = 4.6$, 137 and 54), but the maximum atomic displacement from a mean plane of 0.014 (2) Å (in Cl-Ad-*a*) is not of any chemical significance; C–C = 1.361–1.397 (2–6), mean 1.378 Å, C–C–C = 117.3–122.0 (2–4), mean

120.0° and C–Cl = 1.723 (2) and 1.745 (2) Å. The carbonyl group is almost coplanar with the aromatic ring in H-Ad (angle = 1.4°), but is rotated out of the ring planes by about 20° (in opposite directions) in the two Cl-Ad polymorphs.

The conformations of the central regions of the three adamantylacetophenone molecules are fairly similar to each other, but differ very considerably from those of the previously studied cycloalkylacetophenones (Evans

* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles, torsion angles, and structure factors, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51400 (60 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Trotter, 1988*a,b*). The torsion angle $\phi_1 = C(7)-C(8)-C(9)-C(10)$ again corresponds to a staggered arrangement of bonds, with values of -75 , -64 and -54° in the H-Ad, Cl-Ad-*a* and Cl-Ad-*b* molecules (Table 3), but the adamantyl group is rotated about $C(7)-C(8)$ so that the $C(8)-C(9)$ bond, which lies approximately in the carbonyl plane in the cycloalkyl

Table 3. Molecular conformations, hydrogen abstraction and biradical geometries, and photoproduct ratios for α -adamantylacetophenones

	H-Ad	Cl-Ad- <i>a</i>	Cl-Ad- <i>b</i>
Molecular conformation angles ($^\circ$)			
$\phi_1 = C(7)-C(8)-C(9)-C(10)$	-74.6	-63.6	-54.1
$\phi_2 = O=C(7)-C(8)-C(9)$	81.7	69.9	90.4
$\phi_3 = O=C(7)-C(1)-C(6)$	-2.4	20.0	-18.3
Hydrogen abstraction			
Ring conformation	Chair	Chair	Chair
d (Å)	2.72	2.53	2.78
τ ($^\circ$)	46	43	62
Δ ($^\circ$)	87	92	77
Biradical geometry			
θ_{pp} ($^\circ$)	62	55	68
% Cyclization	100	100	100
% <i>cis</i> -OH cyclobutanol			
Benzene	25	23	23
Acetonitrile	31	36	36
Solid state	22	0	27*

* Reaction at or near the surface.

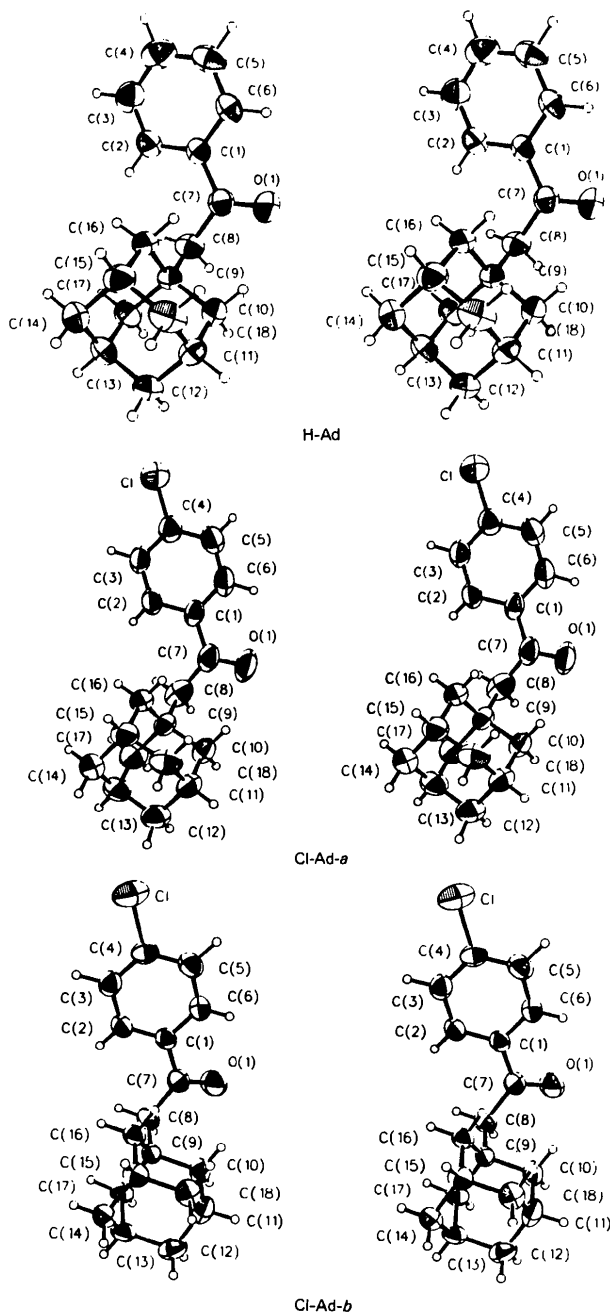


Fig. 1. Stereoviews of the α -1-adamantylacetophenone (H-Ad) molecule, and the α -1-adamantyl-4-chloroacetophenone molecules in the *a* (Cl-Ad-*a*) and *b* (Cl-Ad-*b*) crystal forms.

compounds [$\phi_2 = O=C(7)-C(8)-C(9) \simeq 0^\circ$], is markedly displaced from that plane, with $\phi_2 = 82$, 70 and 90° in the three adamantyl compounds. The principal differences between the Cl-Ad molecules in the *a* and *b* crystal forms are the 20° difference in the ϕ_2 angles, and a difference of about 40° in the orientation of the aromatic rings, with $\phi_3 = O=C(7)-C(1)-C(6) = 20$ and -18° in the two forms ($\simeq 0^\circ$ in the cycloalkyl compounds and in H-Ad).

All three adamantylacetophenones undergo the Norrish type II reaction upon irradiation in solution and in the solid state (Omkehr, 1986). Each molecule has one γ -H atom on C(10) reasonably favourably sited for abstraction by oxygen in a photochemical reaction, with abstraction parameters, d , τ and Δ (Table 3), generally within the ranges found previously. The six-membered rings formed during the abstraction process have chair conformations, in contrast to the mainly boat conformations previously observed in the cycloalkyl derivatives (Evans & Trotter, 1988*a,b*); thus, the geometry of this ring does not seem to be critical to the reaction mechanism.

The interpretation of the photoproduct ratios is considerably simplified relative to the previously studied cycloalkyl derivatives, since, as described in the *Introduction*, cleavage to adamantene is precluded and only two cyclization products are possible, with *cis*- and *trans*-OH groups, respectively [(II) and (III)]. The dimorphic forms of α -adamantyl-*p*-chloroacetophenone show similar solution photoproduct ratios, as expected and α -adamantylacetophenone also shows similar behaviour in solution, with about 25% *cis*-OH (and 75% *trans*-OH) in the non-polar benzene solvent, increasing to about 35% *cis*-OH in the more polar acetonitrile, again as expected (Wagner & Kempainen, 1968).

The photoproduct ratios in the solid-state reactions do not differ very greatly from those in solution (Table 3), again indicating that the photoreactions are governed mainly by intramolecular forces. For H-Ad and Cl-Ad-*b*, the benzene solution and solid-state photoproduct ratios are virtually identical. The interpretation of the results for Cl-Ad-*b* is, however, somewhat ambiguous, as the crystals show clear evidence that the photolysis reaction is occurring at or near the surface (it was possible to remove the photolysed layer with a scalpel and expose the unreacted crystal interior); hence the reaction may not be a true (topochemically controlled) solid-state reaction for Cl-Ad-*b*. For Cl-Ad-*a*, the only solid-state photoproduct is the *trans*-OH cyclobutanol (% *cis*-OH = 0, Table 3).

Molecular models of the two possible types of photoproduct indicate that the *trans*-OH isomer is likely to be more stable, since the *cis*-OH isomer exhibits greater steric interactions between a pseudo-axial aryl substituent on the folded four-membered ring and the adamantyl grouping. This is in accord with the greater amount of *trans*-OH photoproduct, but does require large single-bond rotations of the reactant molecules to produce geometries suitable for cyclization. The reason for the decrease in the % *cis*-OH photoproduct for Cl-Ad-*a* is not clear, although various speculations can be made based on minor differences

between Cl-Ad-*a* and Cl-Ad-*b* in torsion angles and angles between the biradical *p*-orbitals (Table 3) (Evans, Omkaram, Scheffer & Trotter, 1986).

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Structure of Mixed Crystals of Benzoic Acid and *p*-Fluorobenzoic Acid, and their Energy Evaluation by Empirical Potential Functions

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Abstract

'Solid-solution type' mixed crystals of benzoic acid and *p*-fluorobenzoic acid were obtained as phases that were completely different from either of the pure crystals of the two components. The structures of the mixed crystals for two different molar ratios were determined by the X-ray method, and stability of the new mixed crystalline phases was evaluated on the basis of empirical potential-energy calculations. (C₇H₆O₂)_{0.268}·(C₇H₅FO₂)_{0.732}, *M_r* = 135.29, monoclinic, *P*2₁/*c*, *a* = 5.092 (1), *b* = 5.511 (1), *c* = 22.519 (4) Å, β = 94.86 (1)°, *V* = 629.6 Å³, *Z* = 4, *D_x* = 1.427 Mg m⁻³,

λ(Cu Kα) = 1.54178 Å, μ = 0.988 mm⁻¹, *F*(000) = 271.52, *T* = 293 K, *R*(*F*) = 0.051 for 911 unique reflections. (C₇H₆O₂)_{0.553}·(C₇H₅FO₂)_{0.447}, *M_r* = 130.09, monoclinic, *P*2₁/*c*, *a* = 5.184 (1), *b* = 5.474 (1), *c* = 22.086 (2) Å, β = 94.05 (1)°, *V* = 625.2 Å³, *Z* = 4, *D_x* = 1.382 Mg m⁻³, λ(Cu Kα) = 1.54178 Å, μ = 0.835 mm⁻¹, *F*(000) = 261.0, *T* = 293 K, *R*(*F*) = 0.054 for 838 unique reflections.

Introduction

Mixed crystals of fluoride and non-fluoride compounds are thought to be good materials for the study of the differences and similarities between the properties of F and H atoms in organic compounds of biological and

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