

Crystal Structures, Chiralities and Photochemistry of Two Polymorphs of L-Prolinolium α -Adamantylacetophenone-*p*-carboxylate

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Abstract

The absolute stereochemical course of the photochemical rearrangement reactions of α -adamantylacetophenones has been studied by crystal structure analyses of two polymorphs of L-prolinolium α -adamantylacetophenone-*p*-carboxylate and of a crystal containing the major photoproduct, and by correlation of the crystal structure data with photochemical behaviour. Crystal data are: $T = 295$ K, Cu $K\alpha$, $\lambda = 1.54178$ Å. L-Prolinolium α -adamantylacetophenone-4-carboxylate, $C_{24}H_{33}NO_4$, $C_5H_{12}NO^+ \cdot C_{19}H_{21}O_3^-$, $M_r = 399.53$; needle form, $P2_12_12_1$, $a = 17.266$ (2), $b = 19.292$ (3), $c = 6.3739$ (9) Å, $Z = 4$, $R = 0.041$ for 1583 reflections with $I > 3\sigma(I)$; plate form, $P2_12_12_1$, $a = 11.798$ (1), $b = 43.563$ (3), $c = 8.4434$ (8) Å, $Z = 8$ (two molecules per asymmetric unit), $R = 0.056$ for 3565 reflections. Photoproduct (crystals are a 1:1 complex of reactant and photoproduct), $C_{48}H_{68}N_2O_9$ ($C_{24}H_{33}NO_4 \cdot C_{24}H_{33}NO_4 \cdot H_2O$), $M_r = 817.08$, $P2_12_12_1$, $a = 11.021$ (2), $b = 56.481$ (8), $c = 6.840$ (1) Å, $Z = 4$, $R = 0.10$ for 1920 reflections. The two polymorphs of the adamantylacetophenone derivative contain molecules with dimensions and conformations similar to those of previously studied analogues. Both polymorphs have chiral space groups, with the absolute chirality determined from that of the (known) L-prolinolium cation. The needle form of the material ($Z = 4$) contains only one conformational enantiomer of the adamantylacetophenone anion; in the plate form ($Z = 8$), however, the anion exists in both conformational chiralities, as crystallographically independent units. The observation of a large enantiomeric excess in the photoproduct derived from the needle form and a much reduced excess in that derived from the plate form can be correlated with these structural observations. The absolute chirality of the photoproduct from the needle form has been correlated with the absolute chirality of the reactant via a proposed reaction pathway.

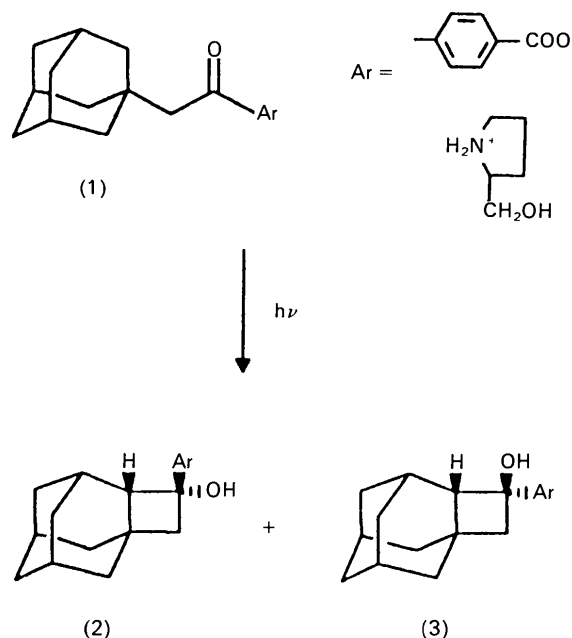
Introduction

When a material crystallizes in a chiral space group such as $P2_12_12_1$, a single crystal usually contains only

one of the two enantiomeric molecules, whether the chirality of the molecule is fixed *via* the bonding scheme or is associated with a particular conformation adopted in the solid state. In the latter case, the possibility then exists of converting this chiral conformation to fixed chirality (*i.e.* an optically active product) by carrying out a photochemical reaction in the crystalline state (Evans *et al.*, 1986; Evans & Trotter, 1989*a,b*); this possibility is necessarily excluded for photochemical reactions of materials crystallizing in non-chiral space groups.

However, even in a chiral space group it is still possible for both enantiomeric forms of a molecule to be present as crystallographically independent units. In such a case, optical activity in a photoproduct would not necessarily be precluded, as in the non-chiral case, but, nevertheless, could only arise as a result of different rates of reaction for the two enantiomeric conformers due to their differing (chiral) environments.

An example of this phenomenon has been investigated and is reported here. Structural and photochemical studies of α -adamantylacetophenones



(Evans & Trotter, 1989*a,b*) have been extended to include two polymorphs of the L-prolinolium* salt of the 4-carboxylate derivative (1) (needles and plates) and of the major photoproduct (2) derived from (1) (needles). In each case, the presence of the L-prolinolium cation has allowed the absolute stereochemistry of the structure to be assigned. The polymorphic forms of (1) differ in an important respect: in (1) (needles), only one enantiomeric conformation of the anion (the photoreactive moiety) is present, whereas in (1) (plates), both conformational enantiomers are present.

Experimental

Data, measured on a Rigaku AFC6-S diffractometer, are summarized in Table 1. For the photoproduct, the only crystals which could be obtained were weakly diffracting thin plates subject to severe lamellar twinning. After several attempts, data were collected from one such crystal; however, the long *b* axis, coupled with the presence of several large satellites, meant that significant overlap of satellite reflections could not be prevented, even with the ω -scan measuring routine. In spite of the poor data, the structure was important enough to persevere with the crystal analysis. All three structures were solved by direct methods and refined by full-matrix least-squares procedures, with $w = 1/\sigma^2(F)$. In (1) (needles), the asymmetric unit consists of one cation-anion pair; in (1) (plates), the unique portion of the structure contains two independent cation-anion pairs. The photoproduct crystal was found to have an asymmetric unit containing two prolinolium cations, one photoproduct anion and one anion of the unreacted adamantylacetophenone; in the latter stages of refinement, a peak was observed in a difference map of this structure, which was interpreted as a water molecule of crystallization. Because of the relatively small number of observed data for the photoproduct crystal, both phenyl rings and the adamantyl group of the reactant molecule were refined as rigid bodies with individual isotropic thermal parameters for the component atoms. All other non-H atoms in the three structures were refined anisotropically. H atoms were mainly placed in calculated sites, except for some of those involved in hydrogen bonds, which were refined [(1), needles] or placed from difference maps (photoproduct); water H atoms were not located. Scattering factors were from *International Tables for X-ray Crystallography* (1974), computer programs as supplied in *TEXSAN* (Molecular Structure Corporation, 1989). In each case, no attempt was made to refine the enantiomeric structures, the absolute chiralities being assigned by

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

| Compound | (1) | | |
|--|---|---|---|
| | Needles | Plates | (1).(2).H ₂ O |
| Crystal data | | | |
| Formula | C ₂₄ H ₃₃ NO ₄ | C ₂₄ H ₃₃ NO ₄ | C ₄₈ H ₆₈ N ₂ O ₉ |
| M.p (K) | 401–403 | 389–391 | – |
| <i>M_r</i> | 399.53 | 399.53 | 817.08 |
| Dimensions | 0.35 × 0.05 × 0.05 | 0.4 × 0.4 × 0.15 | 0.35 × 0.2 × 0.05 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | <i>P</i> 2 ₁ 2 ₁ | <i>P</i> 2 ₁ 2 ₁ | <i>P</i> 2 ₁ 2 ₁ |
| <i>a</i> (Å) | 17.266 (2) | 11.798 (1) | 11.021 (2) |
| <i>b</i> (Å) | 19.292 (3) | 43.563 (3) | 56.481 (8) |
| <i>c</i> (Å) | 6.3739 (9) | 8.4434 (8) | 6.840 (1) |
| <i>V</i> (Å ³) | 2123 (1) | 4340 (1) | 4258 (2) |
| <i>Z</i> | 4 | 8 | 4 |
| <i>D_c</i> (g cm ⁻³) | 1.25 | 1.22 | 1.28 |
| <i>F</i> (000) | 864 | 1728 | 1768 |
| μ (cm ⁻¹) | 6.4 | 6.2 | 6.6 |
| Data collection | | | |
| Reflections for cell | | | |
| Number | 25 | 24 | 22 |
| 2 θ (°) | 31–53 | 88–98 | 15–42 |
| 2 θ_{max} (°) | 155.4 | 155.1 | 155.3 |
| Scan type | ω -2 θ | ω -2 θ | ω |
| ω scan width (°) | | | |
| <i>a</i> + <i>b</i> tan θ | | | |
| <i>a</i> | 0.79 | 1.00 | 0.76 |
| <i>b</i> | 0.20 | 0.20 | 0.20 |
| Scan speed* (° min ⁻¹) | 8.0 | 32.0 | 8.0 |
| <i>h</i> | 0–22 | 0–15 | 0–14 |
| <i>k</i> | 0–24 | 0–55 | 0–72 |
| <i>l</i> | 0–8 | 0–11 | 0–9 |
| Absorption | ψ scans | ψ scans | ψ scans |
| Transmission | 0.76–1.0 | 0.78–1.0 | 0.43–1.0 |
| Total unique reflections | 2480 | 4890 | 5162 |
| Reflections > 3 $\sigma(I)$ | 1583 | 3565 | 1920 |
| % | 63.8 | 72.9 | 37.2 |
| Refinements | | | |
| No. of parameters | 275 | 524 | 375 |
| Data/parameters | 5.75 | 6.8 | 5.12 |
| Δ/σ_{max} | 0.01 | 0.00 | 0.03 |
| $\Delta\rho$ (e Å ⁻³) | –0.18 to +0.17 | –0.21 to +0.20 | –0.36 to +0.56† |
| <i>R</i> | 0.041 | 0.056 | 0.10 |
| <i>wR</i> | 0.047 | 0.057 | 0.097 |
| Extinction (× 10 ³) | 38.0 | 20.1 | 3.73 |
| <i>p</i> factor‡ | 0.03 | 0.00 | 0.01 |

* Up to eight rescans for reflections with $I < 40\sigma(I)$.

† The high values of residual electron density in this structure are associated with the anisotropy of the atoms in the adamantane rigid group.

‡ $\sigma^2(I) = S + 4(B_1 + B_2) + (\rho I)^2$, where *S* = scan, *B*₁, *B*₂ = background counts.

reference to the L-prolinolium cations. Details of the refinements are given in Table 1.

Photolyses of (1) were carried out as previously described (Jones, Scheffer, Trotter & Yang, 1992), with conversions of 70% or higher; optical rotations and enantiomeric excess in the photoproducts were measured for the methyl esters after diazomethane work-up. Attempted crystallization of (2) from acetone after solid-state photolysis of (1) (needles) resulted in the crystals described above (the water presumably being present in the acetone solvent).

* L-Prolinol = (*R*)-2-pyrrolidinemethanol.

Discussion

Final positional parameters are given in Table 2, selected molecular parameters in Table 3 and other data have been deposited.*

The structures and dimensions of all four adamantylacetophenone anions [needles, plates (two anions), and photoproduct complex] (Figs. 1 and 2, Table 3) are very similar to those in related materials (Evans & Trotter, 1989a); the acetophenone carbonyl groups are all rotated out of the planes of the aromatic rings by small amounts 3–13.5°. The anion of the photoproduct (Fig. 2) also has normal geometry (Evans & Trotter, 1989b), with a folded four-membered ring (torsion angles ± 24 – 26°) and a pseudo-axial OH substituent [*trans* to the H atom across the newly-formed C(12)—C(2) bond]. The prolinolium cations also have normal geometries, with non-planar five-membered rings. All the structures exhibit systems of hydrogen bonds involving all active H atoms (Table 4).

Photochemistry of (1)

The carboxylic acid salt (1) undergoes a Norrish type II reaction on photolysis to give the cyclobutanol derivative (2) as the major product (85%), with smaller amounts of the isomer (3) (15%) (Jones *et al.*, 1992). Interestingly, (1) is dimorphic, giving plate-like crystals initially on crystallization from acetone, with needle-shaped crystals then being obtained from the mother liquor. Irradiation of the needle crystals (solid-state) gives (2) as the major photoproduct, in 97% optical purity; the plate crystals also give (2), but with only 12% enantiomeric excess. Solution photolysis gives photoproducts with no optical activity.

One γ -H atom [on C(2)] in each adamantylacetophenone anion (the anion in the needles, both anions in the plates) is favourably cited for abstraction by carbonyl oxygen in a photochemical reaction, with d , ω , Δ and θ parameters (Table 5) close to the usual values, and chair geometries for the six-membered rings formed during the abstraction process (Evans & Trotter, 1989b). The only significant difference is that the two independent anions in the plate crystals are of opposite conformational chirality in the region of the photoreactive centre, with O=C—CH₂—C(β) torsion angles +85.4 (7) and –81.9 (7)°, and OC—CH₂—C(β)—C(γ) of –65.3 (6) and +62.6 (6)°, respectively (Table 5).

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry, and packing diagrams have been deposited with the IUCr (Reference: BR0026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional and equivalent isotropic thermal (\AA^2) parameters

| | $B_{eq} = (8/3)\pi^2 \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$ | | | |
|---------------|---|-------------|-------------|----------|
| | x | y | z | B_{eq} |
| (1) (needles) | | | | |
| O(12) | 0.8896 (2) | 0.6280 (1) | 0.8016 (6) | 5.9 (2) |
| O(19) | 0.8915 (2) | 0.9989 (1) | 0.5883 (4) | 4.7 (1) |
| O(20) | 0.8948 (2) | 0.9440 (1) | 0.2823 (4) | 4.3 (1) |
| O(26) | 0.9120 (2) | 1.1205 (2) | 0.3859 (5) | 5.9 (2) |
| N(21) | 0.8919 (2) | 1.0470 (2) | –0.0049 (6) | 3.0 (1) |
| C(1) | 0.7262 (2) | 0.6409 (2) | 1.0291 (6) | 2.5 (1) |
| C(2) | 0.7264 (2) | 0.5646 (2) | 0.9745 (6) | 3.3 (2) |
| C(3) | 0.6437 (2) | 0.5377 (2) | 0.9414 (7) | 3.9 (2) |
| C(4) | 0.6085 (3) | 0.5770 (2) | 0.7605 (7) | 4.5 (2) |
| C(5) | 0.6053 (2) | 0.6536 (2) | 0.8134 (7) | 4.1 (2) |
| C(6) | 0.5582 (2) | 0.6653 (2) | 1.0098 (8) | 4.8 (2) |
| C(7) | 0.5943 (2) | 0.6248 (2) | 1.1908 (7) | 4.0 (2) |
| C(8) | 0.6774 (2) | 0.6515 (2) | 1.2267 (7) | 3.8 (2) |
| C(9) | 0.6885 (2) | 0.6811 (2) | 0.8487 (6) | 3.5 (2) |
| C(10) | 0.5961 (2) | 0.5489 (2) | 1.1383 (7) | 4.4 (2) |
| C(11) | 0.8092 (2) | 0.6673 (2) | 1.0758 (6) | 3.3 (2) |
| C(12) | 0.8573 (2) | 0.6769 (2) | 0.8816 (7) | 3.5 (2) |
| C(13) | 0.8651 (2) | 0.7477 (2) | 0.7837 (6) | 2.9 (2) |
| C(14) | 0.8438 (2) | 0.8085 (2) | 0.8861 (6) | 3.2 (2) |
| C(15) | 0.8541 (2) | 0.8716 (2) | 0.7887 (6) | 3.0 (2) |
| C(16) | 0.8832 (2) | 0.8760 (2) | 0.5869 (6) | 2.7 (1) |
| C(17) | 0.9031 (2) | 0.8153 (2) | 0.4844 (6) | 3.3 (2) |
| C(18) | 0.8949 (2) | 0.7520 (2) | 0.5827 (6) | 3.3 (2) |
| C(19) | 0.8908 (2) | 0.9456 (2) | 0.4782 (6) | 3.2 (2) |
| C(20) | 0.9457 (2) | 1.1081 (2) | 0.0197 (7) | 3.5 (2) |
| C(22) | 0.8119 (2) | 1.0750 (2) | –0.0103 (8) | 4.7 (2) |
| C(23) | 0.8198 (3) | 1.1452 (2) | –0.105 (1) | 6.8 (3) |
| C(24) | 0.8982 (3) | 1.1700 (2) | –0.0516 (8) | 5.1 (2) |
| C(25) | 0.9737 (3) | 1.1123 (3) | 0.2437 (8) | 5.2 (2) |
| (1) (plates) | | | | |
| O(12) | 0.8716 (4) | 0.4032 (1) | 0.1354 (5) | 6.4 (3) |
| O(19) | 1.2797 (4) | 0.2976 (1) | 0.4862 (5) | 5.9 (2) |
| O(20) | 1.2243 (3) | 0.27790 (9) | 0.2640 (4) | 4.3 (2) |
| O(26) | 1.4635 (4) | 0.26091 (8) | 0.5211 (5) | 5.0 (2) |
| O(42) | 0.3703 (4) | 0.4051 (1) | 0.3921 (5) | 5.9 (2) |
| O(49) | 0.7712 (4) | 0.29877 (9) | 0.0311 (5) | 5.3 (2) |
| O(50) | 0.6900 (3) | 0.27448 (8) | 0.2403 (4) | 3.7 (2) |
| O(56) | 0.9536 (4) | 0.26376 (8) | 0.0143 (6) | 6.1 (2) |
| N(21) | 1.2544 (4) | 0.2239 (1) | 0.4408 (5) | 3.4 (2) |
| N(51) | 0.7445 (4) | 0.2225 (1) | 0.0742 (5) | 3.5 (2) |
| C(1) | 0.8632 (5) | 0.4387 (1) | 0.4701 (7) | 3.7 (3) |
| C(2) | 0.7398 (5) | 0.4409 (1) | 0.4058 (8) | 5.2 (3) |
| C(3) | 0.6593 (5) | 0.4461 (2) | 0.5438 (8) | 5.5 (3) |
| C(4) | 0.6622 (5) | 0.4201 (2) | 0.6585 (8) | 5.6 (4) |
| C(5) | 0.7803 (6) | 0.4184 (2) | 0.7238 (7) | 5.5 (4) |
| C(6) | 0.8114 (7) | 0.4467 (2) | 0.8076 (8) | 6.7 (4) |
| C(7) | 0.8062 (6) | 0.4734 (1) | 0.6917 (8) | 5.3 (3) |
| C(8) | 0.8921 (6) | 0.4674 (1) | 0.5551 (8) | 5.0 (3) |
| C(9) | 0.8658 (6) | 0.4116 (1) | 0.5889 (8) | 4.7 (3) |
| C(10) | 0.6878 (6) | 0.4751 (1) | 0.6246 (8) | 5.9 (4) |
| C(11) | 0.9501 (5) | 0.4344 (1) | 0.3327 (8) | 4.9 (3) |
| C(12) | 0.9392 (5) | 0.4046 (1) | 0.2438 (7) | 4.3 (3) |
| C(13) | 1.0118 (4) | 0.3774 (1) | 0.2824 (6) | 3.7 (3) |
| C(14) | 1.1020 (4) | 0.3793 (1) | 0.3861 (7) | 3.9 (3) |
| C(15) | 1.1682 (4) | 0.3526 (1) | 0.4151 (7) | 4.0 (3) |
| C(16) | 1.1469 (4) | 0.3262 (1) | 0.3370 (6) | 3.4 (2) |
| C(17) | 1.0588 (5) | 0.3236 (1) | 0.2331 (6) | 4.0 (3) |
| C(18) | 0.9887 (4) | 0.3488 (1) | 0.2075 (6) | 3.9 (3) |
| C(19) | 1.2203 (5) | 0.2975 (1) | 0.3631 (7) | 3.7 (3) |
| C(20) | 1.3716 (4) | 0.2114 (1) | 0.4694 (7) | 3.9 (2) |
| C(22) | 1.1938 (5) | 0.1997 (2) | 0.3443 (7) | 5.2 (3) |
| C(23) | 1.2611 (6) | 0.1704 (1) | 0.3675 (8) | 5.3 (3) |
| C(24) | 1.3778 (5) | 0.1817 (1) | 0.3721 (8) | 4.8 (3) |
| C(25) | 1.4591 (6) | 0.2339 (1) | 0.4244 (7) | 4.7 (3) |
| C(31) | 0.3590 (5) | 0.4389 (1) | 0.0500 (6) | 3.4 (2) |
| C(32) | 0.2411 (5) | 0.4404 (1) | 0.1156 (7) | 4.4 (3) |
| C(33) | 0.1540 (5) | 0.4461 (2) | –0.0155 (8) | 5.4 (3) |
| C(34) | 0.1658 (6) | 0.4194 (2) | –0.1336 (9) | 6.6 (4) |
| C(35) | 0.2832 (6) | 0.4174 (1) | –0.2014 (8) | 4.9 (3) |
| C(36) | 0.3083 (6) | 0.4484 (2) | –0.2884 (7) | 5.9 (4) |

Table 2 (cont.)

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eq} |
|-------|------------|------------|-------------|------------------------|
| C(37) | 0.2990 (6) | 0.4747 (1) | -0.1713 (8) | 5.6 (4) |
| C(38) | 0.3817 (5) | 0.4701 (1) | -0.0384 (8) | 5.3 (3) |
| C(39) | 0.3664 (4) | 0.4132 (1) | -0.0699 (7) | 4.0 (3) |
| C(40) | 0.1801 (6) | 0.4774 (2) | -0.1004 (8) | 6.1 (4) |
| C(41) | 0.4467 (5) | 0.4357 (1) | 0.1834 (8) | 4.9 (3) |
| C(42) | 0.4381 (5) | 0.4068 (1) | 0.2834 (7) | 4.3 (3) |
| C(43) | 0.5087 (4) | 0.3794 (1) | 0.2434 (6) | 3.6 (2) |
| C(44) | 0.5954 (5) | 0.3792 (1) | 0.1321 (7) | 4.6 (3) |
| C(45) | 0.6597 (5) | 0.3541 (1) | 0.1038 (7) | 4.2 (3) |
| C(46) | 0.6371 (5) | 0.3263 (1) | 0.1819 (6) | 3.5 (2) |
| C(47) | 0.5471 (5) | 0.3264 (1) | 0.2903 (6) | 3.5 (2) |
| C(48) | 0.4872 (5) | 0.3528 (1) | 0.3233 (7) | 4.0 (3) |
| C(49) | 0.7074 (5) | 0.2986 (1) | 0.1483 (7) | 4.0 (3) |
| C(50) | 0.8676 (5) | 0.2165 (1) | 0.1161 (6) | 4.0 (2) |
| C(52) | 0.6782 (5) | 0.1978 (1) | 0.1432 (7) | 3.9 (3) |
| C(53) | 0.7494 (6) | 0.1703 (1) | 0.1125 (9) | 5.7 (4) |
| C(54) | 0.8716 (6) | 0.1823 (2) | 0.114 (1) | 7.2 (4) |
| C(55) | 0.9508 (5) | 0.2323 (1) | 0.0044 (7) | 4.6 (3) |

(1),(2).H₂O

| | | | | |
|----------------|-----------|------------|-----------|---------|
| O(2 <i>H</i>) | 0.583 (2) | 0.0322 (3) | 0.823 (2) | 13 (1) |
| O(12) | 1.030 (1) | 0.1234 (1) | 0.457 (1) | 3.1 (5) |
| O(19) | 0.578 (1) | 0.0739 (2) | 1.042 (2) | 4.1 (6) |
| O(20) | 0.715 (1) | 0.0783 (2) | 1.270 (2) | 3.8 (6) |
| O(26) | 0.557 (1) | 0.0521 (2) | 0.459 (2) | 3.8 (6) |
| O(42) | 1.539 (2) | 0.1468 (2) | 1.325 (2) | 9 (1) |
| O(49) | 1.123 (1) | 0.0848 (2) | 0.668 (2) | 3.4 (6) |
| O(50) | 1.165 (1) | 0.0653 (2) | 0.937 (2) | 4.0 (6) |
| O(56) | 1.022 (1) | 0.0318 (2) | 0.799 (2) | 4.6 (7) |
| N(21) | 0.372 (1) | 0.0524 (2) | 0.169 (2) | 3.3 (7) |
| N(51) | 0.919 (1) | 0.0628 (2) | 0.489 (2) | 3.9 (8) |
| C(1) | 0.981 (2) | 0.1739 (3) | 0.436 (3) | 3.0 (9) |
| C(2) | 1.013 (2) | 0.1630 (2) | 0.636 (2) | 2.5 (8) |
| C(3) | 1.139 (2) | 0.1702 (3) | 0.698 (3) | 3 (1) |
| C(4) | 1.238 (2) | 0.1670 (3) | 0.545 (3) | 4 (1) |
| C(5) | 1.202 (2) | 0.1801 (3) | 0.361 (2) | 4 (1) |
| C(6) | 1.189 (2) | 0.2073 (3) | 0.397 (3) | 5 (1) |
| C(7) | 1.085 (2) | 0.2099 (2) | 0.552 (3) | 4 (1) |
| C(8) | 0.964 (2) | 0.2016 (2) | 0.461 (3) | 4 (1) |
| C(9) | 1.080 (2) | 0.1712 (2) | 0.287 (3) | 4 (1) |
| C(10) | 1.125 (2) | 0.1979 (3) | 0.732 (3) | 5 (1) |
| C(11) | 0.881 (2) | 0.1559 (3) | 0.416 (2) | 3.3 (9) |
| C(12) | 0.956 (1) | 0.1389 (3) | 0.562 (2) | 3.1 (9) |
| C(19) | 0.678 (2) | 0.0820 (3) | 1.102 (2) | 3 (1) |
| C(20) | 0.344 (2) | 0.0554 (3) | 0.392 (2) | 4 (1) |
| C(22) | 0.377 (2) | 0.0268 (3) | 0.138 (3) | 5 (1) |
| C(23) | 0.294 (2) | 0.0157 (3) | 0.290 (3) | 5 (1) |
| C(24) | 0.315 (2) | 0.0314 (3) | 0.458 (3) | 5 (1) |
| C(25) | 0.452 (2) | 0.0671 (3) | 0.480 (2) | 5 (1) |
| C(41) | 1.627 (2) | 0.1598 (3) | 1.022 (4) | 6 (1) |
| C(42) | 1.541 (2) | 0.1464 (3) | 1.132 (3) | 5 (1) |
| C(49) | 1.175 (2) | 0.0830 (3) | 0.837 (3) | 4 (1) |
| C(50) | 0.845 (1) | 0.0451 (3) | 0.612 (3) | 3 (1) |
| C(52) | 0.974 (2) | 0.0488 (4) | 0.330 (3) | 5 (1) |
| C(53) | 0.912 (4) | 0.0272 (4) | 0.323 (5) | 16 (3) |
| C(54) | 0.841 (2) | 0.0226 (4) | 0.483 (4) | 7 (2) |
| C(55) | 0.901 (2) | 0.0412 (3) | 0.803 (3) | 4 (1) |

Rigid-body atoms

| | | | | |
|-------|------------|------------|-----------|---------|
| C(13) | 0.8785 (8) | 0.1258 (1) | 0.706 (1) | 2.4 (3) |
| C(14) | 0.7711 (9) | 0.1149 (2) | 0.646 (1) | 2.4 (3) |
| C(15) | 0.7060 (7) | 0.1008 (2) | 0.776 (2) | 4.0 (4) |
| C(16) | 0.7484 (9) | 0.0975 (1) | 0.966 (1) | 2.5 (3) |
| C(17) | 0.856 (1) | 0.1083 (2) | 1.026 (1) | 3.6 (4) |
| C(18) | 0.9209 (7) | 0.1225 (1) | 0.896 (1) | 2.0 (3) |
| C(43) | 1.4318 (8) | 0.1330 (1) | 1.047 (2) | 3.7 (4) |
| C(44) | 1.4242 (8) | 0.1286 (2) | 0.846 (2) | 3.2 (4) |
| C(45) | 1.334 (1) | 0.1136 (2) | 0.774 (1) | 4.0 (4) |
| C(46) | 1.2523 (7) | 0.1029 (1) | 0.901 (2) | 2.5 (3) |
| C(47) | 1.2598 (8) | 0.1073 (2) | 1.102 (1) | 4.4 (4) |
| C(48) | 1.350 (1) | 0.1223 (2) | 1.174 (1) | 3.8 (4) |
| C(31) | 1.611 (1) | 0.1864 (1) | 1.006 (2) | 5.2 (5) |
| C(32) | 1.622 (1) | 0.1980 (2) | 1.209 (1) | 6.5 (5) |
| C(38) | 1.710 (1) | 0.1965 (2) | 0.870 (2) | 9.1 (7) |
| C(39) | 1.485 (1) | 0.1916 (2) | 0.919 (2) | 6.2 (5) |

Table 2 (cont.)

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eq} |
|-------|------------|------------|-----------|------------------------|
| C(33) | 1.605 (1) | 0.2249 (2) | 1.190 (1) | 7.1 (6) |
| C(37) | 1.6929 (9) | 0.2234 (2) | 0.850 (2) | 7.9 (6) |
| C(35) | 1.4680 (8) | 0.2186 (2) | 0.900 (2) | 7.8 (6) |
| C(40) | 1.7036 (9) | 0.2350 (2) | 1.054 (2) | 8.3 (6) |
| C(36) | 1.567 (1) | 0.2287 (2) | 0.764 (1) | 11.4 (8) |
| C(34) | 1.4787 (9) | 0.2302 (2) | 1.103 (2) | 7.6 (6) |

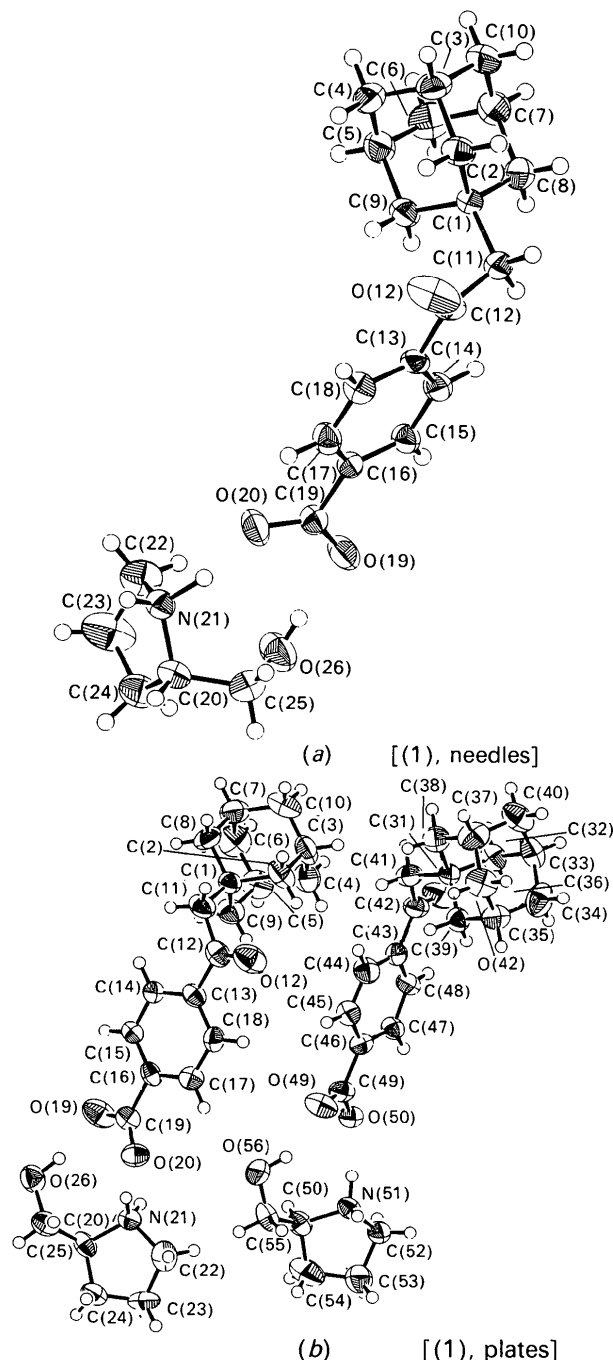


Fig. 1. (a) The cation-anion pair in (1) (needles) and (b) the two independent cations and anions in (1) (plates); 50% thermal probability ellipsoids.

Table 3. Selected bond lengths (Å) and angles (°)

| | (1) (needles) | (1) (plates) | (1) [(1).(2).H ₂ O] | (2) [(1).(2).H ₂ O] |
|---------------------------|------------------|------------------|--------------------------------|--------------------------------|
| Adamantyl group | | | | |
| C—C | 1.503–1.548 (6) | 1.47–1.58 (1) | 1.54 | 1.47–1.59 (2) |
| C—C—C | 108.0–111.8 (3) | 106.6–112.7 (5) | 109.5 | 103–117 (1) |
| Ad—CH ₂ | 1.549 (5) | 1.536, 1.559 (9) | 1.51 (2) | — |
| C—CH ₂ —C | 113.2 (3) | 114.7, 116.0 (5) | 119 (2) | — |
| Four-membered ring | | | | |
| C—C | — | — | — | 1.51–1.61 (2) |
| C—C—C | — | — | — | 84–89 (1) |
| C—C—C—C | — | — | — | ± 24–26 (1) |
| Carbonyl group | | | | |
| C=O | 1.210 (5) | 1.215, 1.220 (8) | 1.32 (2) | C—OH 1.40 (2) |
| C—CO | 1.502, 1.507 (6) | 1.494–1.519 (8) | 1.43, 154 (3) | C(ar)—C(OH) 1.50 (2) |
| Angles at CO | | | | |
| O=C—C(ar)—C(ar) | 119.5–120.4 (4) | 118.5–121.7 (5) | 112–125 (2) | — |
| | 13.5 (5) | –9.8, 5.0 (8) | –3 (2) | HO—C—C(ar)—C(ar) – 82 (1) |
| Aromatic ring | | | | |
| C—C | 1.378–1.390 (5) | 1.348–1.424 (8) | 1.395 | 1.395 |
| C—C—C | 118.1–123.1 (4) | 116.6–122.5 (5) | 120 | 120 |
| C—COO | 1.516 (5) | 1.536, 1.492 (8) | 1.48 (2) | 1.49 (2) |
| Carboxyl group | | | | |
| C—O | 1.246, 1.251 (5) | 1.197–1.321 (7) | 1.21, 1.29 (2) | 1.24, 1.26 (2) |
| C—C—O | 116.0, 118.4 (3) | 115.5–120.2 (5) | 117, 120 (2) | 118, 120 (2) |
| O—C—O | 125.5 (4) | 124.1, 124.6 (5) | 122 (2) | 122 (2) |
| Prolinol | | | | |
| N—C | 1.485, 1.509 (5) | 1.453–1.518 (7) | — | 1.47–1.56 (2) |
| C—C | 1.476–1.518 (7) | 1.461–1.537 (9) | — | 1.37–1.55 (3) |
| C—O | 1.408 (6) | 1.435, 1.372 (7) | — | 1.43, 1.45 (2) |
| C—N—C | 106.9 (3) | 105.6, 107.0 (4) | — | 105, 106 (1) |
| Angles at C(ring) | 104.5–108.1 (4) | 101.6–108.0 (5) | — | 101–115 (2) |
| Angles at C(exo) | 109.7–114.5 (4) | 111.3–115.5 (5) | — | 106–117 (2) |

Table 4. Hydrogen bond distances (Å)

| O...H—Donor | O...D | O...H | H—D |
|---------------------------------|-----------|-------|------|
| (1) (needles) | | | |
| O(19)...H—O(26) | 2.699 (4) | 1.81 | 0.89 |
| O(19)...H—N(21') | 2.754 (5) | 1.93 | 0.85 |
| O(20)...H—N(21) | 2.703 (4) | 1.61 | 1.11 |
| (1) (plates) | | | |
| O(19)...H—O(26) | 2.711 (6) | 1.76 | 0.97 |
| O(49)...H—O(56) | 2.642 (6) | 1.78 | 0.95 |
| O(20)...H—N(21) | 2.809 (6) | 1.87 | 0.96 |
| O(20)...H—N(51 ^{iv}) | 2.865 (6) | 1.90 | 0.96 |
| O(50)...H—N(21 ⁱⁱⁱ) | 2.799 (5) | 1.90 | 0.95 |
| O(50)...H—N(51) | 2.739 (5) | 1.81 | 0.95 |
| (1).(2).H₂O | | | |
| O(19)...H—O(water) | 2.79 (2) | — | — |
| O(26)...H—O(water) | 2.75 (2) | — | — |
| O(20)...H—O(26) | 2.62 (2) | 1.71 | 1.00 |
| O(49)...H—O(12) | 2.81 (1) | 1.66 | 1.19 |
| O(50)...H—O(56) | 2.64 (2) | 1.66 | 1.07 |
| O(19)...H—N(21') | 2.71 (2) | 1.77 | 0.95 |
| O(20)...H—N(51') | 2.84 (2) | 2.03 | 0.95 |
| O(49)...H—N(51) | 2.85 (2) | 1.92 | 0.96 |
| O(50)...H—N(21 ^{iv}) | 2.88 (2) | 1.95 | 0.95 |

Symmetry codes: (i) $x, y, 1+z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (iv) $1+x, y, 1+z$.

Since the absolute stereochemistry of anion (1) is now known, the reaction pathways (leading to four possible photoproducts) can be derived. If the (reasonable) assumption is made that the biradical inter-

Table 5. Hydrogen abstraction parameters in (1)*

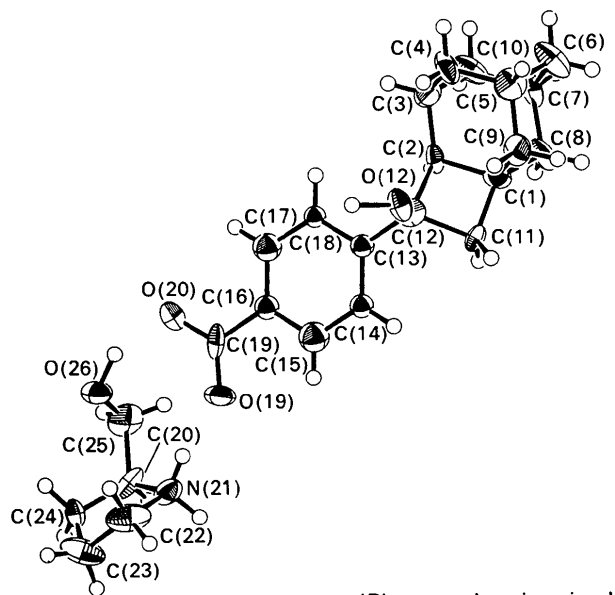
| | Needles | Plates | (1).(2).H ₂ O |
|-----------------------------------|-----------|-----------|--------------------------|
| | | Mol. 1 | Mol. 2 |
| O...H(γ) (Å) | 2.70 | 2.69 | 2.67 |
| O=C—CH ₂ —C(β) (°) | –82.0 (4) | +85.4 (7) | –81.9 (7) |
| OC—CH ₂ —C(β)—C(γ) (°) | +75.6 (4) | –65.3 (6) | +62.6 (6) |
| ω (°) | 46 | 54 | 54 |
| Δ (°) | 87 | 84 | 83 |
| θ (°) | 118 | 115 | 115 |

* O...H(γ) = O(12)...H(2) etc.
ω = angle between O...H(γ) vector and the plane of the carbonyl group.
Δ = C=O...H(γ).
θ = O...H(γ)—C(γ).

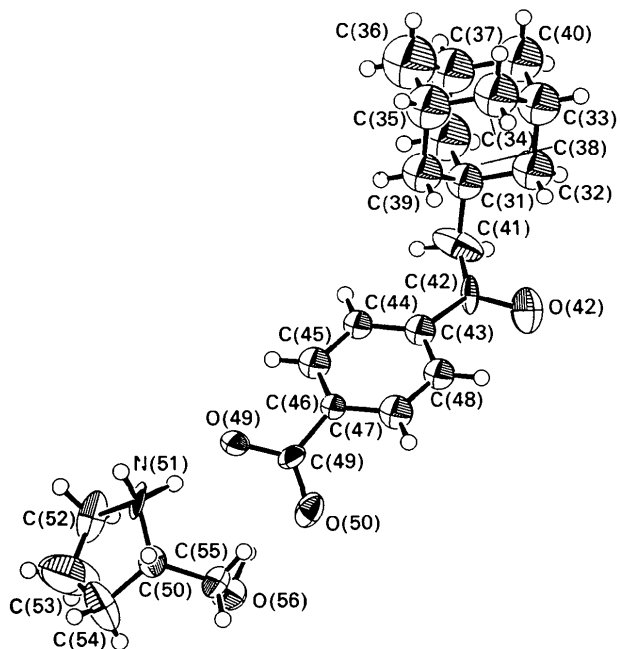
mediate has a conformation fairly similar to that of reactant (1), the pathways leading to closure of the *p*-orbital lobes *a* and *b* to form photoproducts are as detailed in Fig. 3 and Table 6 [the absolute stereochemistry depicted is that of (1) (needles)]. The major photoproduct from (1) (needles) is (2) (85% yield, 97% enantiomeric excess), which is formed by lobe closure *a'b*).

Photoproduct (2) has the OH group pseudo-axial on the folded four-membered ring, *trans* to the H atom on C(2); this is the sterically preferred product, since it has the bulky aryl substituent in the less-crowded pseudo-equatorial site. The most

straightforward pathway, involving closure of the adjacent *a* and *b* lobes, would give the more sterically hindered product (3') [the enantiomer of (3), which would be formed by *a'b'* closure]. The two remaining pathways, *ab'* and *a'b*, would give the enantiomers (2') and (2), the latter being that observed. Hence,



(a) (Photoproduct in mixed crystal)



(b) [(1), in mixed crystal]

Fig. 2. (a) The photoproduct anion (2) and an associated L-prolinolium cation in (1). (2).H₂O and (b) the unreacted anion (1) and an associated cation; water of crystallization not shown, 50% thermal probability ellipsoids.

Table 6. Angles (°) relevant to reaction pathways for (1) (needles)

| p-Orbital lobes† | | Torsion angles* | | | Photoproduct‡ |
|------------------|-----------|-----------------|------------------|----------------|----------------------------------|
| <i>a</i> | <i>b</i> | φ_1 | φ_γ | φ_{CO} | |
| <i>a</i> | <i>b</i> | +76 | -93 | +7 | <i>R</i> - <i>cis</i> -OH (3') |
| <i>a</i> | <i>b'</i> | +76 | -93 | -173 | <i>S</i> - <i>trans</i> -OH (2') |
| <i>a'</i> | <i>b</i> | +76 | +87 | +7 | <i>R</i> - <i>trans</i> -OH (2) |
| <i>a'</i> | <i>b'</i> | +76 | +87 | -173 | <i>S</i> - <i>cis</i> -OH (3) |

* $\varphi_1 = C(12)-C(11)-C(1)-C(2)$; $\varphi_\gamma = p_\gamma-C(2)-C(1)-C(11) = C(11)-C(1)-C(2)-C(3) - 90$; $\varphi_{CO} = p_{CO}-C(12)-C(11)-C(1) = C(13)-C(12)-C(11)-C(1) + 90$.

† See Fig. 3.

‡ (2) is the major solid-state photoproduct; (2') is the enantiomer of (2). *cis/trans* indicate the configuration of OH relative to the H atom on C(2); *R/S* indicate the absolute configuration at C(12).

the pathway leading to the observed product (2) (via *a'b* closure) involves rotation of *ca* 100° about the C(1)—C(11) bond, changing the φ_1 torsion angle from +76° [in (1), Table 6] to -25° [in (2)], and reduction of the C(2)⋯C(12) distance from 3.19 (1) Å in (1) to the bonded distance of 1.58 (2) Å in (2). Pathway *ab'* would involve rotation of 180° about C(11)—C(12), followed by closure of lobes *a* and *b'* to produce (2') (the enantiomer of the observed product). It may therefore be inferred that rotation about C(1)—C(11) to produce the sterically favourable *trans*-OH photoproduct (2) is the preferred (more energetically favourable) pathway.

These observations differ from those for the related 4-chloro- α -(3-methyladamantyl)acetophenone (Evans & Trotter, 1989*b*), where the major

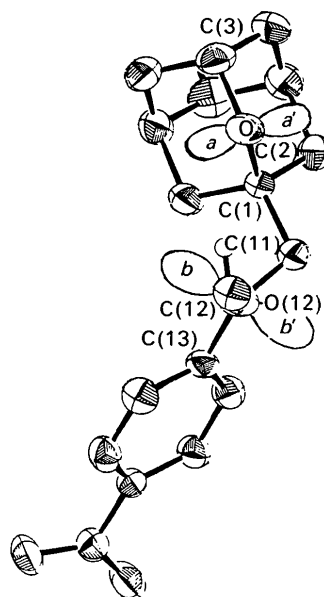


Fig. 3. Schematic drawing of the proposed biradical in the solid-state photolysis of (1) (needles), showing the singly occupied *p*-orbitals.

product is the *cis*-OH isomer derived from the simplest *ab* pathway (absolute stereochemistries were not assigned, but the asymmetry resulting from the 3-methyl substituent allowed assignment of the reaction pathways on the basis of the different regioisomeric photoproducts). The differing behaviours may be rationalized in terms of the interactions of the adamantyl groups with the environments in the crystals. In (1), rotation about the C(1)—C(11) bond is a relatively low-energy process, since the adamantyl group is close to spherical in shape. In the 3-methyl derivative, however, the bulky methyl substituent will tend to hinder rotation of the adamantyl group and thus favour the product resulting from minimum motion in the crystal.

Irradiation of (1) (plates) yields products similar to those from the needle crystals, but with a much reduced enantiomeric excess (12%). Since crystals of (1) (plates) contain both conformational enantiomorphs of the adamantylacetophenone anion, the 12% enantiomeric excess must result from a difference in the rate of reaction of the two enantiomers, due to their differing chiral surroundings.

Optical rotations (Jones *et al.*, 1992) indicate that the photoproduct in 12% excess is (2') [the enantiomer of (2)], which is most likely formed from the enantiomer of (1), which is opposite in chirality to that in the needle crystals, *i.e.* the lower numbered molecule of (1) in the plate crystals (Fig. 1 and Table 2). Inspection of non-bonded contact distances reveals no readily apparent rationalization for this phenomenon.

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Crystal Studies of Musk Compounds. VIII.* Structures of Five Homologues of Musk Phantolid†

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Abstract

The crystal structures of 6-acetyl-2-ethyl-1,1,3,3,5-pentamethylindan (3), 6-formyl-1,1,2,3,3,5-hexamethylindan (4), 5-acetyl-1,1,2,3,3-pentamethylindan (5), 5-acetyl-1,1,2,3,6-pentamethylindan (6) and 5-acetyl-1,1,3,3,6-pentamethylindan (7) have been established by X-ray diffraction. (4) is a strong musk, whilst (6) and (7) have only a weak musk odour. The quality of musks (3) and (5) is not available. (4) and (7) have two and three molecules in the asymmetric unit,

respectively; in both cases, no extra crystallographic symmetry could be detected. Some of the structures described show disorder in the cyclopentene ring and/or in the acyl group. This manifests itself in relatively high displacement parameters and in anomalous bond distances and angles. In two cases [(3) and (6)], a quasiplanar cyclopentene ring is observed. The data are discussed in the light of the necessity of coplanarity of the active group with a phenyl ring for the occurrence of a musk odour. With respect to recent studies dealing with the structure–activity relationships of musk compounds, the most striking observations are that the acetyl group is invariably facing the methyl group at C6 and that the alkyl group at C2 is invariably in the equatorial position.

Introduction

In part III of this series (De Ridder & Schenk, 1991), we reported the crystal structures of Musk Phantolid (1)

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