The Crystal and Molecular Structure of (Z)-2-(p-Nitrobenzoyloxy)-3-phenyl-2-penten-4-one

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The enol-ester derivative of acetylacetone, (Z)-2-(p-nitrobenzoyloxy)-3-phenyl-2-penten-4-one, is orthorhombic, space group *Pbca*. At *ca* −150°C, $a = 7.213$ (1), $b = 32.882$ (3) and $c = 13.055$ (2) Å, $Z = 8$. Diffraction intensities were measured with monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation, for a crystal cooled to *ca* −150°C, to a resolution of $\sin\theta/\lambda \leq 0.904$ Å^{-1}. Block-diagonal least-squares refinement of 277 variables and 7235 reflexions resulted in $R = 0.082$ and $R_w = 0.100$. $C_{18}H_{15}NO_5$ is representative of a series of enol-esters for which an intramolecular O-acyl migration has been demonstrated to occur in solution. The molecular conformation determined from this analysis displays a short intramolecular non-bonded contact between the two carbonyl groups, $O(4)\cdots C(1) = 2.862$ Å, which is consistent with the interaction of these two atoms in the proposed rearrangement mechanism. The geometry displayed by the interacting groups in the known examples of short intramolecular contacts between carbonyl groups is highly constrained by the nature of the chemical linkage between the carbonyl groups. Previous examples of such interactions display geometry with the molecular backbone linking the carbonyl groups in an eclipsed conformation; however, the title compound, which has somewhat more conformational freedom, displays a staggered geometry that is well suited to O-acyl migration through an intramolecular *anti* addition intermediate; the dihedral angle $C(4)O(4)C(1)C(11)$ is 176.7°.

Introduction

O-Acyl transfer has been reported to occur in solution for a series of 2-acyloxy-2-alken-4-ones (Mannschreck & Dvorak, 1973). An intramolecular *O*-acyl shift mechanism, depicted in (I), has been proposed by the above authors based on their interpretation of NMR data.

(I)
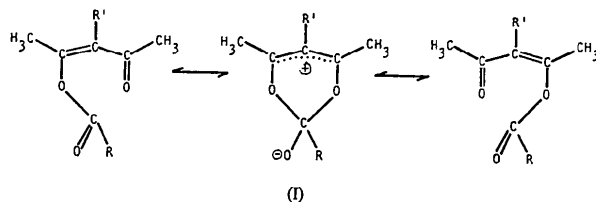
A single-crystal structure determination of (Z)-2-(p-nitrobenzoyloxy)-3-phenyl-2-penten-4-one was undertaken to determine whether the conformation of the molecule was consistent with the proposed mechanism.

Experimental

The title compound crystallizes in space group *Pbca* with (at *ca* −150°C) $a = 7.213$ (1), $b = 32.882$ (3), $c = 13.055$ (2) Å, obtained by least squares (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with the automatically centred 2θ values for 60 reflexions in the angular range $30.0 \leq 2\theta \leq 41.4°$ (Mo $K\alpha$, $\lambda = 0.71069$ Å). The asymmetric unit contains one molecule, $C_{18}H_{15}NO_5$, which gives $D_x = 1.396$ g cm^{-3} (*ca* −150°C).

A $0.32 \times 0.35 \times 0.38$ mm parallelepiped enclosed in a thin-walled glass capillary was maintained at *ca* −150°C (Syntex LT-1 low-temperature device) for the measurement of intensities (with monochromated Mo $K\alpha$ radiation) on a Syntex $P\bar{1}$ autodiffractometer in an ω scan mode for which the scan rate was allowed to vary as a function of maximum peak intensity from 2.0 to 24.0° min^{-1}; a scan range of 0.75° was measured and background intensity was measured on each side of the reflexion for one half the total scan time. Three reflexions, which were monitored periodically, remained constant to within 2.8% of their initial intensities. Of the 9541 unique data ($\sin\theta/\lambda \leq 0.904$ Å^{-1}), 5949 were classified as observed [$I \geq 1.5\sigma(I)$]. Lorentz and polarization corrections were applied; absorption corrections were not deemed necessary.

Structure determination and refinement

The structure was solved by direct methods.* The H atoms were located from difference maps. The atomic coordinates, anisotropic temperature factors for all C, N and O atoms, isotropic temperature factors for H atoms and a single scale factor were refined by block-diagonal least squares. The blocks were constructed such that the parameters associated with: [phenyl ring 1], [the NO₂ moiety], [C(1), O(1) and O(2)], [C(2) and methyl group 2], [phenyl ring 3], [C(3), C(4), O(4) and methyl group 4], and the scale factor were contained in individual blocks. In addition to the data classified as observed, those for which the calculated intensity was greater than the 1.5σ cut-off also contributed to

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* Unless otherwise indicated the X-RAY 1972 program library (Stewart *et al.*, 1972) was used for all calculations.

the refinement. In this manner, 7235 empirically weighted data, $\sigma^2(F) = \sigma_0^2(F) + 0.0125(F) + 0.0010(F)^2$, contributed to the refinement of 277 variables to give $R = 0.082$ and $R_w = 0.100$ and an estimated standard deviation in an observation of unit weight of 1.40.*

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* A list of structure factors and bond distances and angles involving H atoms has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31763 (52 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for carbon, nitrogen and oxygen atoms*

	x	y	z
O(1)	2489 (3)	3704 (1)	4097 (2)
O(2)	963 (3)	4038 (1)	5348 (2)
O(4)	−1760 (4)	4029 (1)	3951 (2)
O(141)	5928 (4)	5583 (1)	2588 (2)
O(142)	4616 (3)	5859 (1)	3904 (2)
N(14)	4945 (3)	5566 (1)	3351 (2)
C(1)	2073 (4)	4016 (1)	4517 (2)
C(11)	2750 (4)	4428 (1)	4211 (2)
C(12)	3955 (4)	4453 (1)	3373 (2)
C(13)	4655 (4)	4830 (1)	3073 (2)
C(14)	4127 (4)	5171 (1)	3632 (2)
C(15)	2905 (4)	5157 (1)	4458 (2)
C(16)	2215 (4)	4778 (1)	4743 (2)
C(2)	130 (4)	3681 (1)	5707 (2)
C(2M)	987 (5)	3548 (1)	6692 (2)
C(3)	−1286 (4)	3507 (1)	5199 (2)
C(31)	−2165 (4)	3131 (1)	5620 (2)
C(32)	−1136 (4)	2778 (1)	5784 (2)
C(33)	−1974 (5)	2433 (1)	6208 (2)
C(34)	−3835 (5)	2439 (1)	6479 (2)
C(35)	−4877 (5)	2787 (1)	6299 (2)
C(36)	−4054 (4)	3128 (1)	5866 (2)
C(4)	−1992 (4)	3673 (1)	4206 (2)
C(4M)	−3012 (5)	3389 (1)	3495 (2)

Examination of the data indicated no significant extinction. The atomic coordinates and temperature factors are given in Tables 1–3.

Table 3. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters* ($\times 10^2$) *for hydrogen atoms*

	x	y	z	U
H(12)	425 (6)	417 (1)	288 (3)	3.5 (1.0)
H(13)	547 (5)	484 (1)	248 (3)	2.6 (0.9)
H(15)	256 (5)	542 (1)	483 (3)	1.7 (0.7)
H(16)	143 (5)	475 (1)	526 (3)	1.9 (0.8)
H(21)	235 (8)	337 (2)	683 (4)	7.6 (1.5)
H(22)	102 (7)	371 (4)	721 (4)	6.0 (1.3)
H(23)	18 (7)	327 (1)	720 (4)	5.8 (1.4)
H(32)	17 (5)	278 (1)	547 (3)	2.4 (0.9)
H(33)	−123 (7)	220 (1)	638 (3)	4.8 (1.2)
H(34)	−438 (6)	221 (1)	691 (3)	4.0 (1.0)
H(35)	−625 (7)	277 (1)	664 (4)	4.6 (1.1)
H(36)	−476 (6)	333 (1)	562 (3)	3.9 (1.2)
H(41)	−443 (9)	334 (2)	358 (5)	8.2 (1.9)
H(42)	−276 (6)	340 (1)	267 (4)	4.7 (1.4)
H(43)	−263 (8)	304 (2)	356 (4)	7.9 (1.8)

Discussion

A stereoscopic projection of the molecule (Johnson, 1965) and the labelling scheme are presented in Fig. 1. The observed conformation is interesting in terms of the mechanism proposed to describe the O-acyl migration (Mannschreck & Dvorak, 1973) [depicted above, (I)], and similarly the interaction proposed to explain the unusual stability of the *cis* isomer of the enol acetates of acetylacetone (Awang, 1973). The observed conformation is clearly consistent with an interaction between O(4) of the carbonyl group and C(1) of the ester moiety. The O(4)–C(1) distance, 2.862 (7) Å, compares fa-

Table 2. *Anisotropic temperature factors* ($\times 10^2$) *for carbon, nitrogen and oxygen atoms*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	3.75 (12)	1.86 (7)	3.43 (10)	−0.01 (7)	1.26 (9)	−0.36 (7)
O(2)	2.94 (10)	1.99 (7)	2.20 (8)	−0.43 (7)	0.64 (7)	−0.20 (6)
O(4)	5.44 (15)	2.41 (9)	3.51 (11)	−0.71 (9)	−1.00 (11)	0.88 (8)
O(141)	4.58 (14)	2.74 (9)	5.05 (14)	−0.12 (10)	2.52 (12)	0.48 (10)
O(142)	4.05 (12)	1.90 (8)	3.42 (10)	−0.12 (8)	−0.11 (9)	−0.09 (7)
N(14)	2.34 (10)	1.94 (8)	3.23 (11)	0.06 (7)	0.18 (9)	0.37 (8)
C(1)	2.25 (11)	1.96 (9)	2.11 (10)	−0.03 (8)	0.23 (8)	0.03 (8)
C(11)	1.90 (10)	1.75 (8)	2.11 (10)	0.06 (7)	0.00 (8)	−0.02 (7)
C(12)	2.45 (11)	1.94 (9)	2.31 (10)	−0.02 (8)	0.42 (9)	−0.13 (8)
C(13)	2.46 (11)	2.09 (10)	2.38 (11)	−0.01 (8)	0.53 (9)	0.07 (8)
C(14)	1.88 (10)	1.79 (8)	2.51 (11)	0.03 (8)	−0.07 (8)	0.21 (8)
C(15)	2.01 (10)	1.88 (9)	2.38 (10)	0.24 (8)	0.02 (8)	−0.06 (8)
C(16)	1.93 (10)	1.88 (9)	2.16 (10)	0.18 (7)	0.19 (8)	0.01 (7)
C(2)	2.47 (11)	1.95 (9)	1.98 (10)	−0.16 (8)	0.40 (9)	−0.07 (7)
C(2M)	3.30 (14)	2.68 (11)	2.21 (11)	−0.30 (10)	−0.30 (10)	−0.05 (9)
C(3)	2.53 (11)	1.83 (9)	1.96 (10)	−0.15 (8)	0.22 (8)	0.09 (7)
C(31)	2.55 (11)	1.78 (8)	1.91 (10)	−0.10 (8)	0.17 (8)	−0.05 (7)
C(32)	2.87 (13)	2.11 (10)	2.80 (12)	0.22 (9)	0.01 (10)	0.06 (9)
C(33)	3.53 (15)	1.97 (10)	3.43 (14)	0.21 (10)	−0.35 (12)	0.43 (9)
C(34)	3.89 (16)	2.10 (10)	2.62 (12)	−0.49 (10)	−0.08 (11)	0.34 (9)
C(35)	3.10 (14)	2.20 (10)	2.98 (13)	−0.34 (10)	0.56 (11)	0.13 (9)
C(36)	2.69 (12)	1.76 (9)	2.87 (12)	0.04 (8)	0.55 (10)	0.03 (8)
C(4)	2.63 (12)	2.38 (10)	2.34 (11)	−0.10 (9)	0.10 (10)	0.26 (8)
C(4M)	3.22 (14)	2.84 (12)	2.49 (12)	−0.33 (10)	−0.41 (11)	0.03 (9)

vourably with those reported for phenylazotribenzoyl-ethylene, PATBM, (Pendergrass, Curtin & Paul, 1972), a compound known to undergo solid-state rearrange-ment, and with that reported for cis-1,2-dibenzoyl-ethylene, DBE, and its di-p-chlorobenzene derivative (Rabinovich, Schmidt & Shaked, 1970); the former has been reported to undergo a photochemical intra-molecular rearrangement (Zimmerman, Dürr, Givens & Lewis, 1967).

The molecular geometry giving rise to the close $O(A)\cdots C(B)$ intramolecular non-bonded contact dis-tances between carbonyl groups A and B differs significantly in this structure from that reported for PATBM and DBE. The differences reflect the con-straints imposed by the chemical structure of the back-bone linking the carbonyl groups. The number of bonded atoms linking $O(A)$ to $C(B)$ in PATBM is four, in DBE five and in this structure six [including $O(A)$ and $C(B)$]. In the previously reported examples, the carbonyl group A and the atoms linking it to carbonyl group B, including $C(B)$, are essentially coplanar and furthermore the plane they define is very nearly per-pendicular to the usual four-atom plane associated with carbonyl group B. Thus the dihedral angle $C(A)O(A)C(B)C(L)$ is very nearly zero [$C(L)$ is the atom bonded to atom $C(B)$ in the backbone between the carbonyl groups A and B]. Clearly the six-atom linkage presented in this investigation cannot adopt the planar conformation described above. As can be seen from Fig. 1, the alternative conformation is inter-esting in that instead of the eclipsed bonds $C(A)$–$O(A)$ with $C(L)$–$C(B)$, the conformation is staggered: the

$C(A)O(A)C(B)O(L)$ dihedral angle is $75 \cdot 7°$. The staggered geometry gives rise to a second dihedral angle, $C(4)O(4)C(1)C(11)$ of $176 \cdot 7°$, characteristic of the geometry suitable for anti addition along the line joining $O(4)$ and $C(1)$.

The short non-bonded intramolecular contact be-tween the two carbonyl groups has resulted in signif-icant nonplanarity in the 2-penten-4-one moiety; the dihedral angle $C(2)C(3)C(4)C(4M)$ is $156 \cdot 7°$. The planarity of the double bond is undisturbed [dihedral angle $C(2M)C(2)C(3)C(4)$, $179 \cdot 5°$]. The conformation is further characterized by the dihedral angles presented in Table 4.

Table 4. Selected dihedral angles (°)

C(11)C(1)O(2)C(2)	176·9	C(3)C(4)O(4)O(2)	19·1
C(1)O(2)C(2)C(3)	−73·4	C(2)O(2)C(1)O(4)	80·1
C(2)C(3)C(4)O(4)	−22·8	C(4)O(4)C(1)O(2)	75·7
C(2)C(3)C(31)C(32)	−59·3	C(4)O(4)C(1)C(11)	176·7
C(2)C(3)C(4)C(4M)	156·7		
C(2M)C(2)C(3)C(4)	179·5		

While the conformation is consistent with the pro-posed mechanism, the interatomic distances and angles between bonded atoms (Tables 5 and 6) display no indication of any disturbance in the bonding character in either the 2-penten-4-one or the p-nitrobenzoate moiety. The bond distances within the ester moiety are nearly identical with those reported for 2,4-hexadi-ynylene dibenzoate (Hanson, 1975), except for the O–C linkage to the pentene double bond, which is, as ex-pected, shorter than that to a single-bonded C atom.
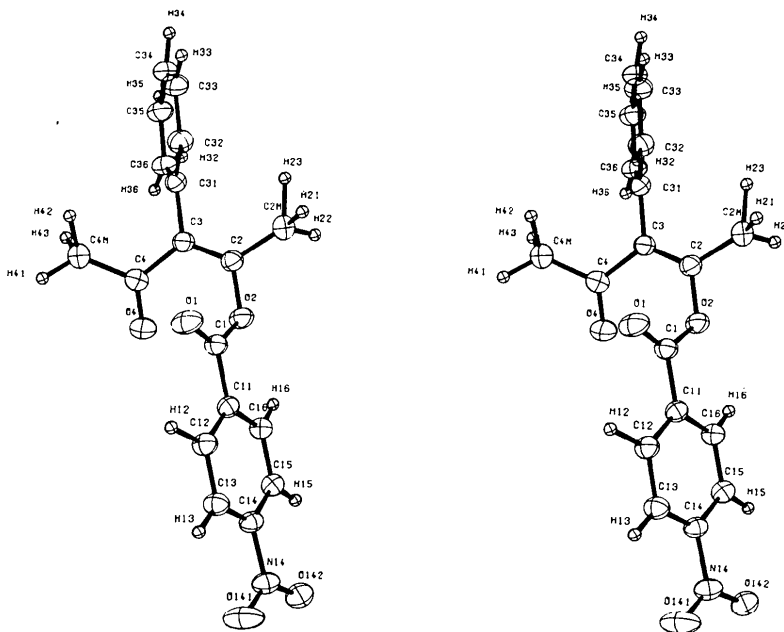

Fig. 1. A stereoscopic projection of (Z)-2-(p-nitrobenzoyloxy)-3-phenyl-2-penten-4-one. The thermal ellipsoids for the carbon, nitrogen and oxygen atoms are depicted for the 75 % probability level. All hydrogen atoms are depicted with uniform isotropic temperature factors ($B = 0 \cdot 75$).

Table 5. Selected distances between carbon, nitrogen and oxygen atoms

(a) Bond distances

C(1)—O(1)	1·202 (3) Å		C(11)–C(12)	1·400 (4) Å
C(1)—O(2)	1·349 (3)		C(11)–C(16)	1·399 (3)
C(1)—C(11)	1·494 (3)		C(12)–C(13)	1·394 (4)
C(2)—O(2)	1·401 (3)		C(13)–C(14)	1·391 (4)
C(2)—C(3)	1·346 (4)		C(14)–C(15)	1·394 (4)
C(2)—C(2M)	1·492 (4)		C(15)–C(16)	1·393 (3)
C(3)—C(4)	1·496 (4)		C(31)–C(32)	1·396 (4)
C(3)—C(31)	1·493 (3)		C(31)–C(36)	1·399 (4)
C(4)—O(4)	1·226 (3)		C(32)–C(33)	1·399 (4)
C(4)—C(4M)	1·510 (4)		C(33)–C(34)	1·389 (5)
C(14)–N(14)	1·475 (3)		C(34)–C(35)	1·388 (4)
N(14)–O(141)	1·225 (4)		C(35)–C(36)	1·389 (4)
N(14)–O(142)	1·226 (3)			

(b) Non-bonded contacts

O(4)–C(1)	2·862 (7) Å		O(4)–O(2)	2·680 (6) Å
C(4)–O(1)	3·237 (8)			

Table 6. Selected interatomic angles

(a) Bond angles (°)

C(11)C(1)O(1)	124·7 (2)		C(1)C(11)C(12)	117·8 (2)
C(11)C(1)O(2)	111·1 (2)		C(1)C(11)C(16)	121·5 (2)
O(1)C(1)O(2)	124·2 (2)		C(12)C(11)C(16)	120·7 (2)
C(1)O(2)C(2)	118·5 (2)		C(11)C(12)C(13)	119·8 (2)
O(2)C(2)C(3)	121·1 (2)		C(12)C(13)C(14)	118·0 (2)
O(2)C(2)C(2M)	110·8 (2)		C(13)C(14)C(15)	123·6 (2)
C(3)C(2)C(2M)	128·0 (2)		C(13)C(14)N(14)	118·1 (2)
C(2)C(3)C(4)	122·0 (2)		C(15)C(14)N(14)	118·3 (2)
C(2)C(3)C(31)	119·5 (2)		C(14)C(15)C(16)	117·5 (2)
C(4)C(3)C(31)	118·5 (2)		C(15)C(16)C(11)	120·4 (2)
C(3)C(4)O(4)	122·5 (2)		C(3)C(31)C(32)	121·3 (2)
C(3)C(4)C(4M)	118·1 (2)		C(3)C(31)C(36)	120·3 (2)
O(4)C(4)C(4M)	119·3 (3)		C(32)C(31)C(36)	118·4 (2)
C(14)N(14)O(141)	118·2 (2)		C(31)C(32)C(33)	120·4 (3)
C(14)N(14)O(142)	118·0 (2)		C(32)C(33)C(34)	120·4 (3)
O(141)N(14)O(142)	123·8 (2)		C(33)C(34)C(35)	119·5 (3)
			C(34)C(35)C(36)	120·1 (3)
			C(35)C(36)C(31)	121·1 (2)

(b) Non-bonded angles (°)

O(2)C(1)O(4)	68·5 (2)
C(1)O(4)C(4)	92·7 (2)

The bond distances in the 2-penten-4-one moiety are precisely those values considered to be representative of a normal C=C double bond and a normal carbonyl group (Kennard, Watson, Allen, Isaacs, Motherwell, Petterson & Town, 1972). The C(3)–C(4) and C(4)–C(4M) distances are equally consistent with expectation. The C(2)–C(2M) distance, which is rather short for a methyl group attached to a C=C double bond, most likely reflects the effects of the electronegativity of the O atom in the ester linkage. The bond distances reported for PATBM and DBE are also generally normal. Thus, while the three systems display conformations suitable for an intramolecular rearrange-

ment, there is no evidence in the observed bonding parameters to indicate a disturbance in the electronic structure of the various compounds.

Table 7. Intermolecular contacts

(a) Between trigonal atoms to 3·5 Å

C(14)–O(141)	3·114 Å		C(32)—C(35)	3·416 Å
N(14)–O(141)	3·146		O(141)–O(142)	3·419
C(1)–O(142)	3·182		C(14)—C(15)	3·458
C(11)–O(142)	3·249		O(141)–O(2)	3·459
C(15)–O(141)	3·336		C(32)—C(34)	3·463
O(2)—O(142)	3·353		C(4)—O(142)	3·469
C(36)–O(142)	3·369		C(12)—O(4)	3·474
C(12)–O(4)	3·380		C(15)—O(4)	3·487
C(3)—O(142)	3·390		C(15)—C(15)	3·493
C(14)–C(16)	3·390		O(142)–O(4)	3·496
N(14)–C(16)	3·416			

(b) Between trigonal and tetrahedral atoms to 3·75 Å

O(141)–C(2M)	3·382		O(1)–C(4M)	3·557
C(36)—C(2M)	3·475		O(1)–C(2M)	3·594
O(1)—C(4M)	3·496			

Those interatomic distances between molecular units that are less than 3·75 Å are presented in Table 7. It is apparent that the crystal packing is governed by van der Waals forces.

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