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N,*N*-Dibenzoyl-2-phenylbenzylamine

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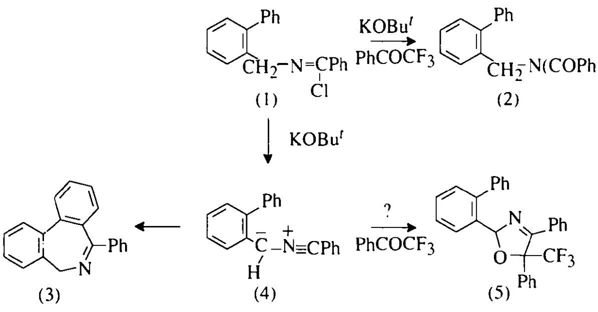
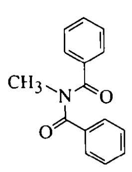
Abstract

The effect on the dibenzamide unit of replacing one methyl H atom in *N*-methyldibenzamide with a 2-biphenyl substituent (giving the title compound, $C_{27}H_{21}NO_2$) is seen primarily in the reduced pyramidalization at the central N atom.

Comment

N,*N*-Dibenzoyl-2-phenylbenzylamine, (2), was produced unexpectedly as the only reaction product in the reaction of *N*-(2-phenylbenzyl)benzimidoyl chloride, (1), with potassium *tert*-butoxide and phenyl trifluoromethyl ketone. The objective of the reaction was that the base should dehydrochlorinate the imidoyl chloride to generate the nitrile ylide (4), which would then react with the ketone in a ($4\pi + 2\pi$) cycloaddition reaction to give the adduct (5). This expectation was based on known chemistry: the nitrile ylide is readily generated by the reaction of compound (1) with potassium *tert*-butoxide (Cullen & Sharp, 1993) and in the absence of trapping reagents it normally cyclizes to give 5-phenyl-7*H*-dibenz[*c*,*e*]azepine, (3), in high yield.





(6)

Structurally, the central NC_3 unit comprising N1, C2, C15 and C22 is planar, with C—N—C angles of 115.97 (14), 118.0 (2) and 125.96 (15)°, the latter involving the two sp^2 carbonyl C atoms C15 and C22 (Fig. 1). The dihedral angles between this central plane and those of the benzoyl phenyl rings are 55.24 (8) and 54.37 (8)°: the mutual inclination of these phenyl rings is 40.40 (8)°. The first phenyl ring of the 2-phenylbenzyl substituent, comprising C3–C8, lies almost orthogonal [80.19 (7)°] to the central NC_3 plane, while the two phenyl rings comprising the substituent are twisted by 62.79 (6)°.

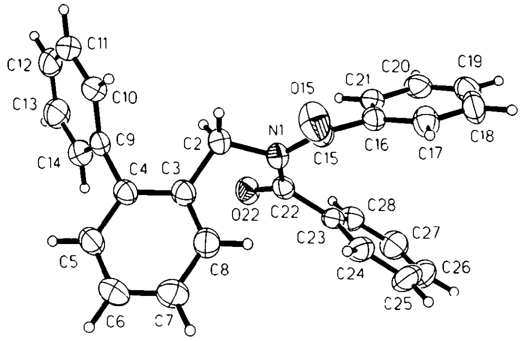


Fig. 1. A view of the molecule with atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces and H atoms are shown as spheres of arbitrary radii.

A search of the Cambridge Structural Database (Allen *et al.*, 1991) showed that the $CN(C{=}O)_2$ grouping has been structurally characterized as part of many larger cyclized systems. However, there are only about 40 examples where no such cyclization is present.

The title compound, (2), is formally derived from (6) by the replacement of one methyl H atom with a 2-biphenyl substituent, and some comparison of the C—N[(C=O)C_6H_5]$_2$ units in these compounds is worthwhile. The bond lengths around the central N atom do not differ significantly between the two molecules but in (6) there is greater pyramidalization at the N atom, which deviates from the plane of the three C atoms to which it is bonded by 0.146 (5) Å (Mizrahi & Niven, 1983), compared with a deviation of only 0.025 (2) Å in (2). Both steric and electronic consequences of the replacement of H by 2-biphenyl may be operating here. Overall, the conformations of (2) and (6) are similar: the orientations about the two N—C(=O) bonds are *cisoid* in both compounds, the angle between the two NCO planes is 40.0 (6) in (2) and 45.4 (4)° in (6), and the rotations of the benzene rings away from the planes of their adjacent amides all lie between 30 and 40°.

Experimental

N-Benzoyl-2-phenylbenzylamine (Cullen & Sharp, 1993) (0.57 g, 2 mmol), dry ether (30 ml) and thionyl chloride

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(10 ml) were heated at reflux under dry nitrogen overnight. The solvent was removed *in vacuo* and the residual *N*-(2-phenylbenzyl)benzimidoyl chloride, (1), was dried under high vacuum for 3 h. Dry tetrahydrofuran (10 ml) and phenyl trifluoromethyl ketone (1.74 g, 10 mmol) were added and the solution was cooled to 273 K. Solid potassium *tert*-butoxide (0.44 g, 4 mmol) was added in one portion under dry nitrogen. The mixture was stirred at 273 K for 30 min. Ammonium chloride solution (20 ml, 25% *w/v*) was then added with vigorous stirring. The mixture was extracted with methylene chloride (3 × 20 ml), the organic fractions were dried over magnesium sulfate and the solvent was removed *in vacuo*. Dry flash chromatography of the residue (silica, ethyl acetate:petrol, 1:49 to 1:9) gave *N,N*-dibenzoyl-2-phenylbenzylamine, (2), as a white crystalline solid (0.41 g, 52%), m.p. 421–422 K (from cyclohexane/toluene). Elemental analysis: found C 83.1, H 5.4, N 3.7%; $C_{27}H_{21}NO_2$ requires C 82.8, H 5.4, N 3.6%. Found *m/z* 391.1577; $C_{27}H_{21}NO_2$ requires *m/z* 391.1572. *m/z* 391 (10%), 286 (29), 165 (30), 105 (49), 69 (100). δ_H(200 MHz) 5.21 (*s*, 2 H), 7.10–7.48 (*m*, 18 H, Ar-H), 7.65–7.70 p.p.m. (*m*, 1H, Ar-H). ν_{max}(Nujol) 1690 cm^{-1} (C=O).

Crystal data

$C_{27}H_{21}NO_2$
$M_r = 391.45$
Monoclinic
$P2_1/n$
$a = 14.8208\,(12)$ Å
$b = 8.1939\,(4)$ Å
$c = 17.4844\,(9)$ Å
$\beta = 91.185\,(4)°$
$V = 2122.9\,(2)$ Å^3
$Z = 4$
$D_x = 1.225$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 12–13°$
$\mu = 0.077$ mm^{-1}
$T = 298\,(2)$ K
Lath
0.74 × 0.26 × 0.10 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
On-line profile fitting (Clegg, 1981) for ω–2θ scans
Absorption correction: none
2762 measured reflections
2762 independent reflections

2080 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 22.44°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0347$
$wR(F^2) = 0.1044$
$S = 1.034$
2762 reflections
272 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.246P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.10$ e Å^{-3}
$\Delta\rho_{min} = -0.11$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0069 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.63248 (10)	0.0579 (2)	0.64208 (8)	0.0599 (4)
C2	0.59020 (14)	0.1864 (2)	0.68869 (10)	0.0703 (5)
C3	0.54839 (12)	0.1245 (2)	0.76115 (10)	0.0589 (5)
C4	0.47444 (11)	0.2060 (2)	0.79182 (9)	0.0569 (5)
C5	0.43663 (13)	0.1453 (3)	0.85836 (11)	0.0705 (6)
C6	0.4707 (2)	0.0083 (3)	0.89433 (11)	0.0812 (6)
C7	0.5430 (2)	−0.0717 (3)	0.86462 (12)	0.0834 (6)
C8	0.58153 (14)	−0.0133 (3)	0.79840 (11)	0.0734 (6)
C9	0.43275 (12)	0.3521 (2)	0.75467 (9)	0.0573 (5)
C10	0.47854 (14)	0.4984 (2)	0.74718 (11)	0.0708 (6)
C11	0.4360 (2)	0.6331 (3)	0.71559 (13)	0.0857 (7)
C12	0.3481 (2)	0.6230 (3)	0.69067 (14)	0.0936 (8)
C13	0.3020 (2)	0.4791 (3)	0.69690 (14)	0.0929 (7)
C14	0.34420 (13)	0.3448 (3)	0.72862 (12)	0.0733 (6)
C15	0.72581 (13)	0.0647 (2)	0.63252 (11)	0.0648 (5)
O15	0.77380 (10)	0.1259 (2)	0.68213 (9)	0.0970 (5)
C16	0.76385 (11)	0.0087 (2)	0.55947 (10)	0.0579 (5)
C17	0.85015 (13)	−0.0577 (3)	0.56027 (13)	0.0809 (6)
C18	0.8886 (2)	−0.1069 (3)	0.4928 (2)	0.0958 (8)
C19	0.8428 (2)	−0.0875 (3)	0.4249 (2)	0.0953 (8)
C20	0.7582 (2)	−0.0194 (3)	0.42304 (12)	0.0829 (7)
C21	0.71849 (13)	0.0282 (2)	0.48999 (10)	0.0635 (5)
C22	0.57335 (12)	−0.0556 (2)	0.60807 (9)	0.0566 (5)
O22	0.49313 (9)	−0.0245 (2)	0.60376 (8)	0.0759 (4)
C23	0.60929 (11)	−0.2160 (2)	0.58379 (9)	0.0557 (5)
C24	0.67166 (13)	−0.3025 (2)	0.62744 (12)	0.0702 (5)
C25	0.7009 (2)	−0.4528 (3)	0.6016 (2)	0.0976 (8)
C26	0.6691 (2)	−0.5135 (3)	0.5329 (2)	0.1064 (9)
C27	0.6057 (2)	−0.4295 (3)	0.4911 (2)	0.0959 (7)
C28	0.57537 (14)	−0.2825 (3)	0.51648 (11)	0.0731 (6)

Table 2. *Selected geometric parameters (Å, °)*

N1—C2	1.478 (2)	C15—O15	1.218 (2)
N1—C15	1.398 (2)	C15—C16	1.480 (2)
N1—C22	1.402 (2)	C22—O22	1.217 (2)
C2—C3	1.510 (2)	C22—C23	1.484 (3)
C4—C9	1.490 (3)		
C2—N1—C15	118.0 (2)	O15—C15—C16	121.0 (2)
C2—N1—C22	115.97 (14)	N1—C15—C16	119.1 (2)
C15—N1—C22	125.96 (15)	O22—C22—N1	119.3 (2)
N1—C2—C3	114.2 (2)	O22—C22—C23	121.6 (2)
O15—C15—N1	119.7 (2)	N1—C22—C23	119.0 (2)
C15—N1—C2—C3	−115.4 (2)		
C22—N1—C2—C3	67.8 (2)		
N1—C2—C3—C8	28.8 (3)		
N1—C2—C3—C4	−150.9 (2)		
C22—N1—C15—O15	−154.5 (2)		
C2—N1—C15—O15	29.0 (3)		
C22—N1—C15—C16	30.1 (3)		
C2—N1—C15—C16	−146.3 (2)		
O15—C15—C16—C21	−141.5 (2)		
N1—C15—C16—C21	33.7 (3)		
O15—C15—C16—C17	34.9 (3)		
N1—C15—C16—C17	−149.8 (2)		
C15—N1—C22—O22	−160.4 (2)		
C2—N1—C22—O22	16.1 (2)		
C15—N1—C22—C23	24.3 (2)		
C2—N1—C22—C23	−159.17 (15)		
O22—C22—C23—C28	42.9 (2)		
N1—C22—C23—C28	−142.0 (2)		
O22—C22—C23—C24	−134.3 (2)		
N1—C22—C23—C24	40.8 (2)		

Refinement was on F^2, but all negative values of the intensities were lost at a data transfer. H atoms were initially placed in calculated positions. Subsequently they were allowed to ride on their respective C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1326). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.
Cullen, K. E. & Sharp, J. T. (1993). *J. Chem. Soc. Perkin Trans.* 1, pp. 2961–2967.
Mizrahi, V. & Niven, M. L. (1983). *S. Afr. J. Chem.* **36**, 137–142.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL/PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stoe & Cie (1988*a*). *DIF*4. *Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988*b*). *REDU*4. *Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

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The Diels–Alder Adduct of an Enantiopure Sulfinyl Trialkoxycarbonyl Ethene and Cyclopentadiene

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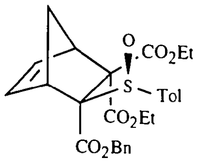
Abstract

The absolute configuration of (1*S*,2*S*,4*R*,*SS*)-2-benzyl 3,3-diethyl 2-(*p*-tolylsulfinyl)bicyclo[2.2.1]hept-5-ene-2,3,3-tricarboxylate, $C_{28}H_{30}O_7S$, has been determined.

Comment

The ability of the sulfinyl group to control the π-facial selectivity in the asymmetric Diels–Alder reaction has provided the impetus for the use of enantiopure α,β-unsaturated sulfoxides as dienophiles. Nevertheless, the low dienophilic reactivity of vinyl sulfoxides determines that other activating groups must be attached to the double bond (Arai, Matsui, Koizumi & Shiro, 1991; Takahashi, Kotsubo & Koizumi, 1991; Carreño, García-Ruano & Urbano, 1992; Fuji *et al.*, 1994). In this sense, sulfinyl maleates (Alonso, Carretero & García-Ruano, 1994) reacted with a variety of dienes in high yields and stereoselectivities. However, the cyclohexenes resulting from the reaction with acyclic dienes evolve quickly at room temperature into cyclohexadienes by non-regioselective pyrolitic elimination of the sulfinyl group. In order to avoid this problem, a triactivated enantiopure vinyl sulfoxide was prepared (Carretero, García-Ruano & Martín Cabrejas, 1995) and the determination of the absolute configuration of its Diels–Alder adduct with cyclopentadiene was performed by X-ray analysis. The molecular structure of this compound, (I), and the atomic numbering scheme are shown in Fig. 1.



(I)

The angle between the carbonyl groups C13—O6 and C10—O4 is −167.5 (5)°, whereas the angle between the sulfinyl group S1—O1 and the carbonyl group C8—O2 is −79.8 (4)°. The angle between the aromatic rings is 132.3 (2)°. An intermolecular hydrogen bond was found [H36···O6^{i} = 2.527 (8), C36···O6^{i} = 3.366 (8) Å, C36—H36···O6^{i} = 150.2 (2)°; symmetry code: (i) $x-1, y, z$].

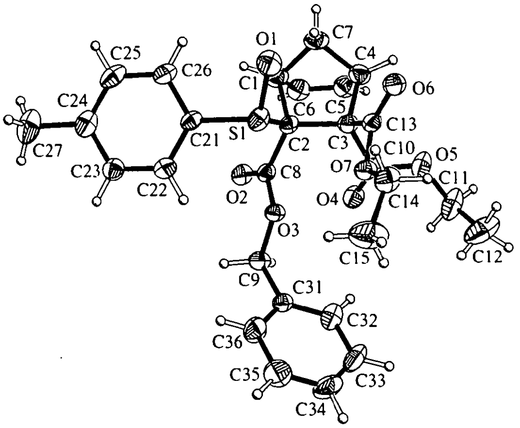


Fig. 1. Molecular structure of the compound showing 20% probability displacement ellipsoids.

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