O(1)—C(2)—C(1′)	110.7 (2)	C(1′)—C(6′)—C(5′)	119.9 (2)
O(1)—C(2)—C(3)	121.4 (2)	O(4)—C(7)—C(6)	114.0 (2)
C(1′)—C(2)—C(3)	127.9 (2)	O(4)—C(7)—C(8)	124.2 (2)
C(1′)—C(2′)—C(3′)	120.7 (2)	C(6)—C(7)—C(8)	121.8 (2)
C(2′)—C(3′)—C(4′)	119.7 (3)	C(7)—C(8)—C(9)	117.3 (2)
C(2)—C(3)—C(4)	122.0 (2)	O(1)—C(9)—C(8)	115.7 (2)
O(2)—C(4)—C(3)	123.4 (2)	O(1)—C(9)—C(10)	121.1 (2)
O(2)—C(4)—C(10)	121.1 (2)	C(8)—C(9)—C(10)	123.2 (2)
C(3)—C(4)—C(10)	115.6 (2)	C(4)—C(10)—C(5)	122.2 (2)
C(3′)—C(4′)—C(5′)	119.9 (3)	C(4)—C(10)—C(9)	120.2 (2)
C(4′)—C(5′)—C(6′)	120.9 (2)	C(5)—C(10)—C(9)	117.6 (2)
O(3)—C(5)—C(6)	119.1 (2)		

Lorentz and polarization corrections were applied. The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The H atoms were located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement was performed for non-H atoms, isotropic for H atoms, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Calculations were performed using *SDP* (Frenz, 1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data including dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71699 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1070]

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3-Bromo-6-methylamino-2′-methoxybenzophenone

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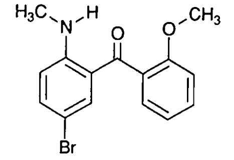
Abstract

The two molecules, *A* and *B*, of $C_{15}H_{14}BrNO_2$ in the asymmetric unit only differ significantly in the dihedral angle O(5)—C(5)—C(1′)—C(2′) [95.1 (3) and 107.9 (3)°, respectively]. The carbonyl O atom and the N atom are connected *via* an intramolecular hydrogen bond.

Comment

In an attempt to protonate 7-bromo-1-methyl-5-(*o*-methoxyphenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one with dilute sulfuric acid we obtained the title compound (I), which was formed on hydrolysis. Thus the conclusion can be drawn that the protonation has to be carried out in the absence of water, for example, with dried hydrochloric acid (Berger, 1993).



(I)

The only significant difference between the two molecules in the asymmetric unit is the angle between the two nearly planar moieties [moiety (1) of molecule *A*: C(11), N(1), C(9*A*), C(9), C(8), C(7), Br(7), C(6), C(5*A*), C(5), O(5); moiety (2) of molecule *A*: C(1′), C(2′), C(3′), C(4′), C(5′), C(6′), O(21′), C(21′); moiety (1) of molecule *B*: C(11*B*), N(1*B*), C(9*AB*), C(9*B*), C(8*B*), C(7*B*), Br(7*B*), C(6*B*), C(5*AB*), C(5*B*), O(5*B*); moiety (2) of molecule *B*: C(1′*B*), C(2′*B*), C(3′*B*), C(4′*B*), C(5′*B*), C(6′*B*), O(21*B*), C(21*B*)]: 83.5 (molecule *A*), 77.3° (molecule *B*).

An intramolecular hydrogen bond is formed between the carbonyl O atom and the N atom: N(1)···O(5) 2.623 (6) Å, N(1)—H(1)···O(5) 133.3 (7)° and N(1*B*)···O(5*B*) 2.675 (6) Å, N(1*B*)—H(1*B*)···O(5*B*) 133.3 (7)°.

The title compound compares well with 2-aminobenzophenone (Antolini, Vezzosi, Battaglia & Corradi, 1985); however, a smaller torsion angle

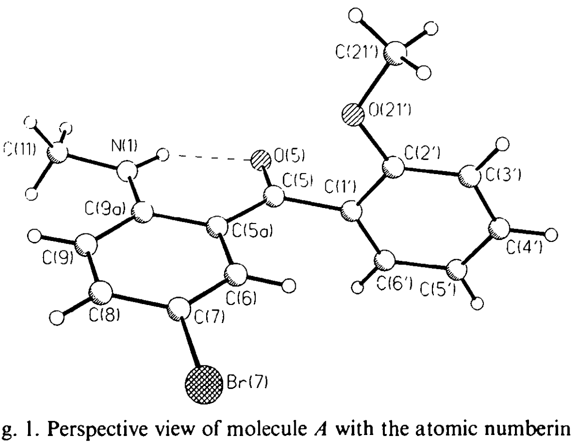


Fig. 1. Perspective view of molecule *A* with the atomic numbering.

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about C(5)—C(1′) ($\Delta\varphi$ 40.5 and 53.3°, respectively) is found as a result of the missing *ortho* substituent.

Experimental

7-Bromo-1-methyl-5-(*o*-methoxyphenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one was dissolved in dilute sulfuric acid at room temperature. After two weeks one single transparent colourless block appeared. After the structure solution, it became apparent that the title compound had been formed upon hydrolysis from the benzodiazepine derivative.

Crystal data

$C_{15}H_{14}BrNO_2$
$M_r = 320.2$
Monoclinic
$P2_1/c$
$a = 20.845$ (4) Å
$b = 7.927$ (1) Å
$c = 17.080$ (3) Å
$\beta = 91.61$ (1)°
$V = 2821.2$ (8) Å^3
$Z = 8$

$D_x = 1.508$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 36.5$–$58.0°$
$\mu = 3.97$ mm^{-1}
$T = 293$ K
Transparent block
0.50 × 0.40 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical
$T_{\min} = 0.68$, $T_{\max} = 0.99$
5427 measured reflections
4137 independent reflections
3996 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.022$
$\theta_{\max} = 60°$
$h = -23 \rightarrow 0$
$k = -8 \rightarrow 2$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 92 min
intensity variation: negligible

Refinement

Refinement on F
$R = 0.037$ [for $F > 4\sigma(F)$]
$wR = 0.050$ [for all reflections]
$S = 5.10$
3996 reflections
362 parameters
$w = 1/[\sigma^2(F) + 0.00003F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}

Extinction correction: empirical, $F^* = F[1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.0017$ (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
N(1)	0.8790 (2)	0.6784 (4)	0.6505 (2)	0.079 (1)
C(11)	0.8985 (3)	0.7281 (7)	0.5731 (2)	0.123 (2)
C(5)	0.8310 (1)	0.5583 (3)	0.7969 (2)	0.048 (1)
O(5)	0.7928 (1)	0.5466 (3)	0.7413 (1)	0.079 (1)
C(5*A*)	0.8947 (1)	0.6301 (3)	0.7895 (2)	0.047 (1)
C(6)	0.9352 (1)	0.6416 (3)	0.8564 (2)	0.052 (1)
C(7)	0.9956 (2)	0.7061 (4)	0.8519 (2)	0.069 (1)
Br(7)	1.0506 (1)	0.7192 (1)	0.9416 (1)	0.112 (1)
C(8)	1.0175 (2)	0.7629 (5)	0.7796 (3)	0.084 (2)
C(9)	0.9791 (2)	0.7543 (5)	0.7144 (3)	0.082 (2)
C(9*A*)	0.9170 (2)	0.6879 (4)	0.7159 (2)	0.060 (1)
C(1′)	0.8088 (1)	0.4950 (3)	0.8748 (2)	0.045 (1)
C(2′)	0.8234 (1)	0.3317 (4)	0.8998 (2)	0.046 (1)
O(21′)	0.8643 (1)	0.2462 (3)	0.8535 (1)	0.063 (1)
C(21′)	0.8737 (2)	0.0697 (4)	0.8682 (3)	0.080 (1)
C(3′)	0.7962 (1)	0.2698 (4)	0.9669 (2)	0.059 (1)
C(4′)	0.7557 (2)	0.3700 (5)	1.0087 (2)	0.071 (1)
C(5′)	0.7412 (2)	0.5305 (5)	0.9852 (2)	0.075 (1)
C(6′)	0.7677 (1)	0.5927 (4)	0.9176 (2)	0.061 (1)
N(1*B*)	0.4693 (1)	0.7710 (3)	0.3883 (2)	0.058 (1)
C(11*B*)	0.4126 (1)	0.8515 (4)	0.4184 (2)	0.068 (1)
C(5*B*)	0.5807 (1)	0.6178 (4)	0.3183 (2)	0.048 (1)
O(5*B*)	0.5426 (1)	0.6772 (3)	0.2699 (1)	0.077 (1)
C(5*AB*)	0.5740 (1)	0.6390 (3)	0.4030 (1)	0.043 (1)
C(6*B*)	0.6237 (1)	0.5868 (3)	0.4532 (1)	0.044 (1)
C(7*B*)	0.6199 (1)	0.6057 (3)	0.5327 (2)	0.049 (1)
Br(7*B*)	0.6904 (1)	0.5435 (1)	0.5998 (1)	0.066 (1)
C(8*B*)	0.5651 (2)	0.6712 (4)	0.5648 (2)	0.056 (1)
C(9*B*)	0.5150 (1)	0.7226 (4)	0.5166 (2)	0.053 (1)
C(9*AB*)	0.5179 (1)	0.7131 (3)	0.4347 (2)	0.045 (1)
C(1′*B*)	0.6382 (1)	0.5260 (4)	0.2890 (1)	0.048 (1)
C(2′*B*)	0.6439 (1)	0.3500 (4)	0.2945 (2)	0.047 (1)
O(21*B*)	0.5942 (1)	0.2693 (3)	0.3291 (1)	0.064 (1)
C(21*B*)	0.5938 (2)	0.0886 (4)	0.3275 (3)	0.081 (1)
C(3′*B*)	0.6969 (1)	0.2698 (4)	0.2651 (2)	0.054 (1)
C(4′*B*)	0.7433 (2)	0.3636 (5)	0.2292 (2)	0.064 (1)
C(5′*B*)	0.7378 (2)	0.5359 (5)	0.2222 (2)	0.069 (1)
C(6′*B*)	0.6850 (1)	0.6152 (4)	0.2522 (2)	0.058 (1)

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

N(1)—C(11)	1.449 (5)	N(1)—C(9*A*)	1.353 (4)
C(5)—O(5)	1.225 (4)	C(5)—C(5*A*)	1.455 (4)
C(5)—C(1′)	1.506 (4)	C(5*A*)—C(6)	1.403 (4)
C(5*A*)—C(9*A*)	1.428 (4)	C(6)—C(7)	1.364 (4)
C(7)—Br(7)	1.891 (4)	C(7)—C(8)	1.402 (6)
C(8)—C(9)	1.355 (6)	C(9)—C(9*A*)	1.399 (5)
C(1′)—C(2′)	1.393 (4)	C(1′)—C(6′)	1.381 (4)
C(2′)—O(21′)	1.360 (3)	C(2′)—C(3′)	1.384 (4)
O(21′)—C(21′)	1.433 (4)	C(3′)—C(4′)	1.372 (5)
C(4′)—C(5′)	1.366 (6)	C(5′)—C(6′)	1.384 (5)
N(1*B*)—C(11*B*)	1.449 (4)	N(1*B*)—C(9*AB*)	1.351 (4)
C(5*B*)—O(5*B*)	1.224 (3)	C(5*B*)—C(5*AB*)	1.468 (4)
C(5*B*)—C(1′*B*)	1.499 (4)	C(5*AB*)—C(6*B*)	1.391 (4)
C(5*AB*)—C(9*AB*)	1.428 (4)	C(6*B*)—C(7*B*)	1.371 (4)
C(7*B*)—Br(7*B*)	1.903 (3)	C(7*B*)—C(8*B*)	1.383 (4)
C(8*B*)—C(9*B*)	1.373 (4)	C(9*B*)—C(9*AB*)	1.402 (4)
C(1′*B*)—C(2′*B*)	1.403 (4)	C(1′*B*)—C(6′*B*)	1.372 (4)
C(2′*B*)—O(21*B*)	1.367 (3)	C(2′*B*)—C(3′*B*)	1.381 (4)
O(21*B*)—C(21*B*)	1.433 (4)	C(3′*B*)—C(4′*B*)	1.378 (4)
C(4′*B*)—C(5′*B*)	1.376 (5)	C(5′*B*)—C(6′*B*)	1.378 (5)
C(11)—N(1)—C(9*A*)	124.4 (4)	O(5)—C(5)—C(5*A*)	122.5 (3)
O(5)—C(5)—C(1′)	116.8 (2)	C(5*A*)—C(5)—C(1′)	120.7 (2)
C(5)—C(5*A*)—C(6)	119.0 (2)	C(5)—C(5*A*)—C(9*A*)	121.5 (2)
C(6)—C(5*A*)—C(9*A*)	119.6 (3)	C(5*A*)—C(6)—C(7)	120.9 (3)
C(6)—C(7)—Br(7)	121.0 (3)	C(6)—C(7)—C(8)	119.6 (3)
Br(7)—C(7)—C(8)	119.4 (3)	C(7)—C(8)—C(9)	120.6 (4)
C(8)—C(9)—C(9*A*)	121.9 (4)	N(1)—C(9*A*)—C(5*A*)	120.8 (3)
N(1)—C(9*A*)—C(9)	121.8 (3)	C(5*A*)—C(9*A*)—C(9)	117.5 (3)
C(5)—C(1′)—C(2′)	120.7 (2)	C(5)—C(1′)—C(6′)	119.4 (3)
C(2′)—C(1′)—C(6′)	119.5 (3)	C(1′)—C(2′)—O(21′)	114.9 (2)
C(1′)—C(2′)—C(3′)	119.5 (3)	O(21′)—C(2′)—C(3′)	125.7 (3)
C(2′)—O(21′)—C(21′)	118.0 (3)	C(2′)—C(3′)—C(4′)	119.9 (3)
C(3′)—C(4′)—C(5′)	121.4 (3)	C(4′)—C(5′)—C(6′)	119.1 (3)
C(1′)—C(6′)—C(5′)	120.7 (3)	C(11*B*)—N(1*B*)—C(9*AB*)	123.2 (3)
O(5*B*)—C(5*B*)—C(5*AB*)	122.9 (3)	O(5*B*)—C(5*B*)—C(1′*B*)	118.1 (2)
C(5*AB*)—C(5*B*)—C(1′*B*)	118.9 (2)	C(5*B*)—C(5*AB*)—C(6*B*)	119.0 (2)
C(5*B*)—C(5*AB*)—C(9*AB*)	121.6 (2)	C(6*B*)—C(5*AB*)—C(9*AB*)	119.5 (2)
C(5*AB*)—C(6*B*)—C(7*B*)	121.0 (2)	C(6*B*)—C(7*B*)—Br(7*B*)	120.2 (2)
C(6*B*)—C(7*B*)—C(8*B*)	120.4 (3)	Br(7*B*)—C(7*B*)—C(8*B*)	119.5 (2)
C(7*B*)—C(8*B*)—C(9*B*)	119.7 (3)	C(8*B*)—C(9*B*)—C(9*AB*)	122.0 (3)
N(1*B*)—C(9*AB*)—C(5*AB*)	121.7 (2)	N(1*B*)—C(9*AB*)—C(9*B*)	121.0 (3)
C(5*AB*)—C(9*AB*)—C(9*B*)	117.3 (2)	C(5*B*)—C(1′*B*)—C(2′*B*)	121.8 (2)
C(5*B*)—C(1′*B*)—C(6′*B*)	119.2 (3)	C(2′*B*)—C(1′*B*)—C(6′*B*)	118.9 (3)

C(1′*B*)—C(2′*B*)—O(21*B*)	115.5 (2)	C(1′*B*)—C(2′*B*)—C(3′*B*)	120.0 (3)
O(21*B*)—C(2′*B*)—C(3′*B*)	124.5 (3)	C(2′*B*)—O(21*B*)—C(21*B*)	117.5 (3)
C(2′*B*)—C(3′*B*)—C(4′*B*)	119.5 (3)	C(3′*B*)—C(4′*B*)—C(5′*B*)	121.1 (3)
C(4′*B*)—C(5′*B*)—C(6′*B*)	119.1 (3)	C(1′*B*)—C(6′*B*)—C(5′*B*)	121.4 (3)

Only coordinates of H atoms attached to N atoms were refined, with distance restraint N—H = 0.90 Å (weight 10^{+8}); $U = 1.2U_{eq}(C_{aromatic})$ or $1.2U_{eq}(N)$ or $1.5U_{eq}(C_{methyl})$; H atoms attached to C atoms were not refined. Refinement was carried out using *SHELXTL* (Sheldrick, 1983).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71750 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1077]

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Ein Zwölfring mit Phosphor(V), Kohlenstoff und Dimethylhydrazin als Ringbausteinen und großen endocyclischen Torsionswinkeln um die N—N-Bindungen

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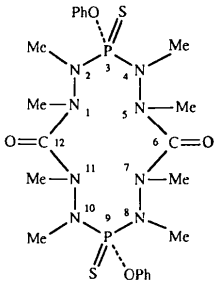
Abstract

1,2,4,5,7,8,10,11-Octamethyl-6,12-dioxo-3,9-diphenoxy-1,2,4,5,7,8,10,11-octaaza-3λ^5,9λ^5-diphosphacyclododecane 3,9-disulfide (1) is the dimer of the expected product of the reaction of bis(1,2-dimethylhydrazido)thiophosphoric acid phenyl ester with ethyl chloroformate. The title compound is the *Z* isomer. The 12-membered ring has a strongly puckered conformation with endocyclic P—N—N—C torsion angles from −84 (1) to −106.8 (9)° and C—N—N—C torsion angles from −73 (1) to −76 (1)°. The mean N—N bond distance of 1.40 (1) Å is at the lower end of the observed range in smaller P^V-hydrazine rings.

Kommentar

Anorganische Phosphor-Hydrazin-Sechsringe werden seit einiger Zeit von uns synthetisiert und Strukturell untersucht. Sie liegen vielfach in einer stabilen Twistkonformation vor. Dies hängt in großem Maße von der Raumbeanspruchung der Ringsubstituenten ab (Engelhardt, Bünger & Viertel, 1984). Da nur sehr wenige Strukturen anorganischer, nicht-alternierender Heterocyclen mit mitlerer Ringgröße bekannt sind, deren Daten im Vergleich mit verwandten Phosphor(V)-Hydrazin-Sechsringen interessant erscheinen, haben wir die Strukturuntersuchung von (1) durchgeführt, das bei der Umsetzung des entsprechenden Thiophosphorsäuredihydrazids mit Chlorameisensäureethylester wider Erwarten als Dimeres isoliert wurde.



(1)

Die asymmetrische Einheit wird durch ein Molekül der Titelverbindung gebildet (Fig. 1). Der Ring ist stark gewellt. Die auf der gleichen Seite des Rings liegenden Phenoxy-Gruppen stehen nahezu axial, die Schwefelatome an den Phosphorringatomen dagegen quasi äquatorial. Besonders auffällig ist die starke Verdrillung um die N—N-Bindungen im Ring. Die Torsionswinkel um diese Bindungen (Tabelle 2) haben verglichen mit analogen Phosphor-Hydrazin-Sechsringen sehr hohe Werte. C(1)—N(1)—N(2)—C(2) −74 (1), C(4)—N(4)—N(5)—C(5) −74 (1), C(7)—N(7)—N(8)—C(8) −73 (1), C(10)—N(10)—N(11)—C(11) −76 (1)°. Die C···C-Kontaktabstände zwischen Methyl-C-Atomen an benachbarten N-Atomen sind dementsprechend mit im Mittel 3,09 (2) Å im Bereich zu erwartender van-der-Waals-Kontakte. In den Sechsringen führen dagegen sterische Wechselwirkungen zwischen diesen Methylgruppen zu einer Begünstigung der Twist-Konformation mit ihren gegenüber der Sessel-Konformation größeren C—N—N—C-Torsionswinkeln. Die N—N-Abstände liegen mit im Mittel 1,40 (1) Å am unteren Ende des Erfahrungsbereichs und sind vergleichbar mit denen in den entsprechenden Sechsringen mit Carbonyl-Baugruppe (Engelhardt & Simon, 1992). Besonders kurze intermolekulare Abstände finden

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