C10—C11	1.368 (3)	S—O63	1.427 (2)
C10—C18	1.425 (3)	S—O62	1.439 (2)
C11—C12	1.396 (3)	S—O61	1.561 (2)
C12—N13	1.315 (3)	O61—C65	1.435 (4)
N13—C19	1.370 (3)	C65—C66	1.463 (6)
C2—N1—C6	108.7 (2)	C12—N13—C19	117.8 (2)
C2—N1—C8	114.1 (2)	C15—C14—C19	120.8 (2)
C6—N1—C8	107.7 (2)	C14—C15—C16	119.8 (2)
C2—N1—H11	112 (2)	C17—C16—O20	125.6 (2)
C6—N1—H11	106 (2)	C17—C16—C15	121.0 (2)
C8—N1—H11	108 (2)	O20—C16—C15	113.4 (2)
N1—C2—C3	109.1 (2)	C16—C17—C18	120.3 (2)
C26—C3—C2	108.9 (2)	C17—C18—C19	118.3 (2)
C26—C3—C4	116.9 (2)	C17—C18—C10	124.8 (2)
C2—C3—C4	108.6 (2)	C19—C18—C10	116.9 (2)
C5—C4—C7	108.8 (2)	N13—C19—C14	117.3 (2)
C5—C4—C3	108.1 (2)	N13—C19—C18	123.0 (2)
C7—C4—C3	109.0 (2)	C14—C19—C18	119.8 (2)
C4—C5—C6	109.5 (2)	C16—O20—C21	118.1 (2)
N1—C6—C5	107.9 (2)	O27—C26—O28	123.9 (3)
C4—C7—C8	109.0 (2)	O27—C26—C3	123.6 (3)
N1—C8—C7	107.3 (2)	O28—C26—C3	112.4 (2)
N1—C8—C9	112.0 (2)	C26—O28—C29	116.5 (3)
C7—C8—C9	114.5 (2)	O28—C29—C30	107.9 (3)
O22—C9—C10	109.8 (2)	O64—S—O63	114.8 (2)
O22—C9—C8	109.3 (2)	O64—S—O62	112.4 (2)
C10—C9—C8	108.5 (2)	O63—S—O62	109.48 (15)
C11—C10—C18	118.4 (2)	O64—S—O61	103.06 (14)
C11—C10—C9	118.5 (2)	O63—S—O61	109.18 (14)
C18—C10—C9	123.0 (2)	O62—S—O61	107.42 (12)
C10—C11—C12	120.6 (2)	C65—O61—S	118.4 (2)
N13—C12—C11	123.3 (2)	O61—C65—C66	107.6 (4)

Most H atoms were found on difference Fourier maps and refined with individual positional parameters. The positions of those on C21, C29, C30, C65 and C66 were calculated and included as riding atoms in the refinement. Isotropic displacement parameters for H atoms were used in the refinement.

Data collection: *KM*-4 *Software*. Cell refinement: *KM*-4 *Software*. Data reduction: *KM*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995), *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93, *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Columnar Stacking of 1,3-Diphenyl-1,2,4-benzotriazin-4(1*H*)-yl Radicals

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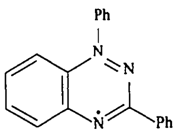
Abstract

The title radicals, $C_{19}H_{14}N_3$, are arranged in columns along the *b* axis in which the almost planar 1,2,4-triazin-4(1*H*)-yl ring and the phenyl ring on C3 of adjacent molecules lie alternately on top of one another. Within the array, the mean interplanar distance is 3.45 Å. However, the centers of the 1,2,4-triazin-4(1*H*)-yl rings, bearing most of the spin population, are 5.50 Å apart. Consequently, there are only very weak intermolecular interactions along the columns, which is in agreement with the results of static magnetic susceptibility measurements.

Comment

Recent studies of magnetic properties of 1,2,4-benzotriazin-4(1*H*)-yl radicals (Mukai, Inoue, Achiwa, Jamali, Krieger & Neugebauer, 1994) directed our attention towards the crystal structure of 1,3-diphenyl-1,2,4-benzotriazin-4(1*H*)-yl which can be considered to be a basic compound in this group of stable free radicals (Blatter & Lukaszewski, 1968; Blatter, 1969; Neugebauer & Umminger, 1980). Moreover, it is of interest to compare the crystal structure of the title compound, (I), with that of the 1-(4-chlorophenyl)-3-phenyl derivative. This stable radical is packed in columns comprising two kinds of radical pairs and shows an extraordinarily large antiferromagnetic exchange interaction, whereas the susceptibility of the title compound follows the Curie–Weiss law (Mukai *et al.*, 1994).



(I)

A view of the title compound, with the atom-numbering scheme, is given in Fig. 1. The molecular structure (Fig. 2) reveals an almost planar, slightly roof-shaped 1,2,4-benzotriazin-4(1*H*)-yl skeleton with N1 −0.044, N4 −0.020, C4a −0.037, C8a −0.043, N2 +0.046, C3 +0.046, C6 +0.025 and C7 +0.038 Å showing the largest displacements out of their least-squares plane. The 3-phenyl substituent also lies close to this plane, the angle between the two ring planes being 10.5°. The phenyl substituent in position 1, on the other hand, is twisted considerably out of the molecular plane by 55.9°, apparently to avoid a steric interaction between H8 and H2′ [distance H8···H2′ = 2.49 (3) Å].

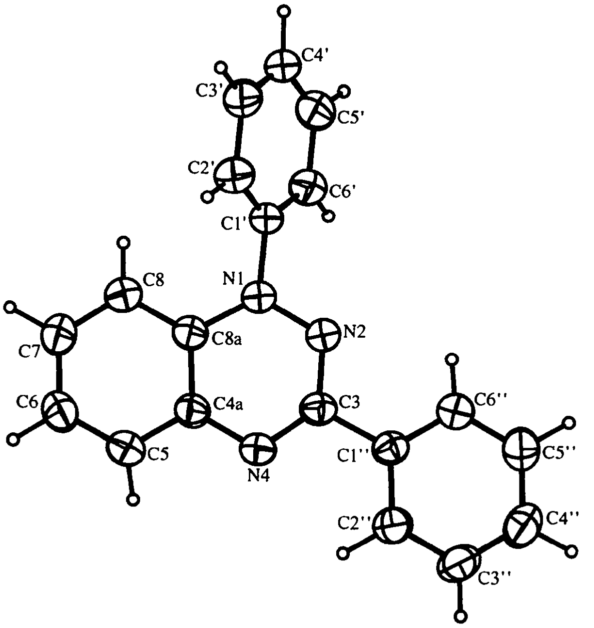


Fig. 1. A view of the 1,3-diphenyl-1,2,4-benzotrazin-4(1*H*)-yl radical with the atom-labeling scheme. Displacement ellipsoids are plotted at the 50% probability level.

In the 1,2,4-triazin-4(1*H*)-yl ring, the delocalization of the unpaired electron is clearly indicated by the bond lengths of the amidrazonyl moiety: N1—N2 1.361 (2), N2—C3 1.337 (2), C3—N4 1.324 (2) Å. As expected, these bond lengths as well as the inner bond angles N1—N2—C3 116.2 (1), N2—C3—N4 127.7 (2), C3—N4—C4a 115.8 (1)° are similar to those of the 1-(4-chlorophenyl) derivative [N1—N2 1.365 (3), N2—C3 1.327 (2), C3—N4 1.315 (3) Å, N1—N2—C3 116.0 (1), N2—C3—N4 128.1 (2), C3—N4—C4a 115.5 (2)°]. The bond distances of the amidrazonyl moiety correspond closely to data of comparable hydrazyl structures, *e.g.* 2,2-diphenyl-1-picrylhydrazyl [N—N 1.334 (6) Å; Williams, 1967], 1,3,5-triphenyl-6-oxoverdazyl [N—N 1.368 (1), C—N 1.330 (1) Å; Neugebauer, Fischer & Krieger, 1993] and 1,3,5,5-tetraphenyl-2,5-dihydro-1*H*-1,2,4-triazolyl [N1—N2 1.338 (2), C3—N2 1.368 (2), C3—N4 1.305 (2) Å; Neugebauer, Fischer & Krieger, 1989]. The notable deviations in the last example are due to the amidrazonyl moiety being bridged by an isopropylidene group to give a five-membered ring system with a predominant localized hydrazyl structure. The title radicals are stacked along the *b* axis. In the columns, the phenyl ring at C3 and the 1,2,4-triazin-4(1*H*)-yl ring lie alternately one on top of the other (Fig. 2). Within the array, the mean interplanar distance is 3.45 Å which can be considered to be a mean distance between adjacent π systems. However, the centers of the 1,2,4-triazin-4(1*H*)-yl rings are 5.50 Å apart [shortest intermolecular contact $C3\cdots C1''^{i}$ 3.603 (3) Å; symmetry code (i) 1.5 − *x*, 0.5 + *y*, 0.5 − *z*]. This packing suggests one-dimensional magnetic properties and only weak antiferromagnetic intermolecular interactions, if any. Indeed, the molar susceptibility of this radical follows the Curie–Weiss law with a Curie constant of 0.375 K emu mol^{-1} and a Weiss constant of −2.2 K in the temperature range 300–7 K. A deviation occurs below 7 K corresponding

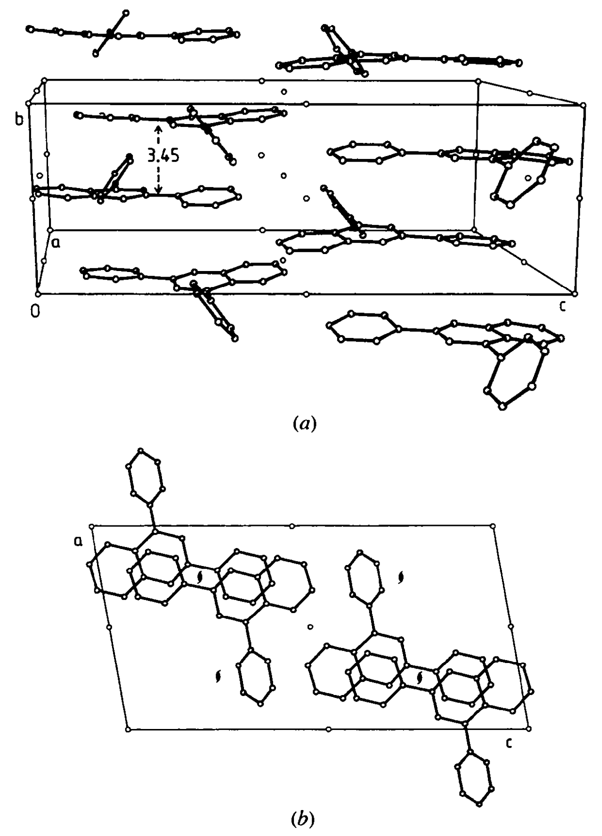


Fig. 2. (*a*) Projection of the title compound showing the columnar arrangement along **b** (interplanar distance in Å). (*b*) Projection down **b** showing the intermolecular overlap between adjacent molecules.

to very weak antiferromagnetic intermolecular interactions at low temperature (Mukai *et al.*, 1994).

Experimental

The title compound (Blatter & Lukaszewski, 1968; Neugebauer & Umminger, 1980) was available in our laboratory. Crystals suitable for X-ray analysis were obtained by repeated recrystallization from methanol.

Crystal data

$C_{19}H_{14}N_3$
$M_r = 284.34$
Monoclinic
$P2_1/n$
$a = 10.477\ (2)$ Å
$b = 6.953\ (1)$ Å
$c = 19.865\ (3)$ Å
$\beta = 99.55\ (2)°$
$V = 1427.1\ (8)$ Å^3
$Z = 4$
$D_x = 1.32$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–14°$
$\mu = 0.075$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.20 × 0.15 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3599 measured reflections
3417 independent reflections
1710 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 27.96°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = -26 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.057$
$wR = 0.050$
$S = 2.187$
1710 reflections
255 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o) + 0.0009\ F_o^2]$

$(\Delta/\sigma)_{\rm max} = 0.015$
$\Delta\rho_{\rm max} = 0.1100$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.1600$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography*

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	$U_{\rm eq}$
N1	0.5268 (1)	0.2138 (2)	0.34231 (7)	0.0419 (4)
N2	0.5594 (1)	0.2107 (2)	0.27881 (7)	0.0422 (4)
C3	0.6859 (2)	0.2061 (3)	0.27608 (9)	0.0382 (5)
N4	0.7834 (1)	0.2027 (2)	0.32789 (7)	0.0422 (4)
C4a	0.7496 (2)	0.1952 (3)	0.39184 (9)	0.0398 (5)
C5	0.8453 (2)	0.1784 (3)	0.4492 (1)	0.0499 (6)
C6	0.8147 (2)	0.1624 (3)	0.5135 (1)	0.0549 (6)
C7	0.6857 (2)	0.1640 (3)	0.5219 (1)	0.0556 (6)
C8	0.5883 (2)	0.1824 (3)	0.46666 (9)	0.0480 (6)
C8a	0.6196 (2)	0.1995 (3)	0.40160 (9)	0.0401 (5)
C1′	0.3908 (2)	0.2134 (3)	0.34283 (9)	0.0428 (5)
C2′	0.3363 (2)	0.3493 (3)	0.3795 (1)	0.0544 (6)
C3′	0.2042 (2)	0.3462 (4)	0.3793 (1)	0.0677 (7)
C4′	0.1280 (2)	0.2126 (4)	0.3426 (1)	0.0732 (8)
C5′	0.1823 (2)	0.0786 (4)	0.3051 (1)	0.0707 (7)
C6′	0.3146 (2)	0.0785 (4)	0.3048 (1)	0.0557 (6)
C1″	0.7170 (2)	0.2029 (3)	0.20561 (9)	0.0386 (5)
C2″	0.8455 (2)	0.2198 (3)	0.1964 (1)	0.0483 (6)
C3″	0.8759 (2)	0.2147 (3)	0.1313 (1)	0.0567 (6)
C4″	0.7818 (2)	0.1916 (3)	0.0757 (1)	0.0573 (6)
C5″	0.6549 (2)	0.1751 (3)	0.0843 (1)	0.0592 (7)
C6″	0.6227 (2)	0.1811 (3)	0.1488 (1)	0.0497 (6)

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

N1—N2	1.361 (2)	C4a—C5	1.393 (2)
N1—C8a	1.401 (2)	C4a—C8a	1.408 (3)
N1—C1′	1.427 (2)	C5—C6	1.372 (3)
N2—C3	1.337 (2)	C6—C7	1.389 (3)
C3—N4	1.324 (2)	C7—C8	1.375 (2)
C3—C1′	1.489 (3)	C8—C8a	1.390 (3)
N4—C4a	1.375 (2)		
N2—N1—C8a	122.2 (1)	N4—C4a—C8a	122.0 (1)
N2—N1—C1′	114.3 (1)	C5—C4a—C8a	118.1 (2)
C8a—N1—C1′	123.3 (1)	C4a—C5—C6	121.4 (2)
N1—N2—C3	116.2 (1)	C5—C6—C7	119.6 (2)
N2—C3—N4	127.7 (2)	C6—C7—C8	120.8 (2)
N2—C3—C1″	114.3 (1)	C7—C8—C8a	119.5 (2)
N4—C3—C1″	118.0 (2)	N1—C8a—C4a	116.0 (2)
C3—N4—C4a	115.8 (1)	N1—C8a—C8	123.4 (2)
N4—C4a—C5	119.9 (2)	C4a—C8a—C8	120.6 (2)
N2—N1—C1′—C6′	50.3 (2)	N2—C3—C1″—C6″	−8.1 (2)
C8a—N1—C1′—C2′	57.9 (2)	N4—C3—C1″—C2″	−7.6 (2)

A well oriented but considerably misplaced structure fragment was obtained by direct phasing of a set of 180 reflections (Sheldrick, 1990). Final structure solution was achieved by geometrical completion of the model followed by suitable translation in the (010) plane, leading to a residual of about 0.20. Subsequent difference Fourier maps revealed all H atoms at expected positions.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: Direct methods *SHELXS*86 (Sheldrick 1990). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIFVAX MolEN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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