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Molecular and Crystal Structure of a Superstable Free Radical, 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl

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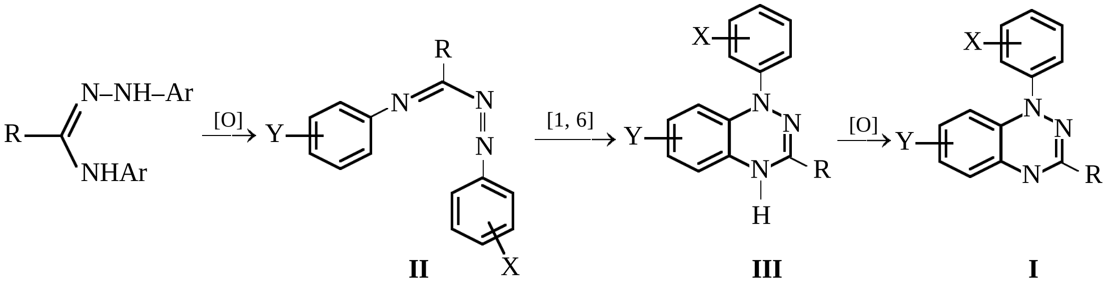
Abstract — The molecular and crystal structure of a superstable free radical, 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl, was studied by single crystal X-ray diffraction. The dihedral angle formed by the *N*-phenyl ring with the heteroring is considerably larger than that formed by the *C*-phenyl ring; two geminal C–N bonds in the dihydrotriazine ring have virtually equal length. In the crystal, the radical molecules form stacks along the 0*b* axis due to π–π interactions of the aromatic fragments of the molecules. The total effect of intermolecular contacts in the crystal leads to formation of a lamellar supramolecular structure.

Among free radicals, much researchers' attention is given to 1,4-dihydro-1,2,4-benzotriazin-4-yl radicals **I** prepared for the first time in 1968 [1]. These radicals show particularly high stability as compared to other N-centered radicals; they also exhibit other specific properties [1–6]. For example, the ESR spectra of 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl **Ia** show certain anomalies [2, 4–6], and the sample prepared at our institute in 1973 still preserves its properties [7].

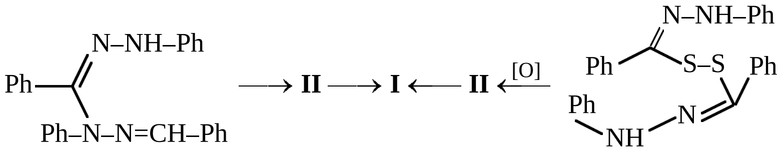
Although synthesis, chemical properties, and spectra of 1,4-dihydro-1,2,4-benzotriazin-4-yl radicals have been reported in numerous papers [1–4, 7–10], only two papers concern the molecular and crystal structure of these compounds [11, 12]. 1,4-Dihydro-1,2,4-benzotriazin-4-yl radicals can be readily prepared by thermolysis of 1,4-diaryl-2-R-1,3,4-triazabutadienes **II** (*C*-arylazo-*N*-arylimines, hereinafter azo imines), as the cyclization products, 1,4-dihydro-1,2,4-benzotriazines **III**, are readily oxidized [1–4, 7–9]. Cyclization of azo imines **II** into benzotriazines **III** is so easy that compounds **II** often cannot be isolated, e.g., in oxidation of amidrazones, especially those containing at the N^3 atom an unsubstituited phenyl group or a phenyl group with donor substituents. Benzotriazines **III** are also very labile and are very readily oxidized to radicals **I** directly in the reaction medium or during recrystallization. Such transformations [scheme (1)] were described for amidrazones containing the following substituents: R = Ph, *t*-Bu, $Z_2P(=O)$ (Z = *i*-PrO), morpholino; X = H, Me, 4-Cl, 4-NO_2; Y = H, Me, OMe [1–4, 7–10].



(1)

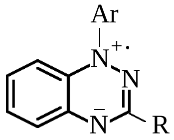
Pyrolysis of 1,4-diphenyl-2-benzylidenehydrazidines [7] and oxidation of bis(α-aminohydrazonobenzyl) disulfide with nitrobenzene [9], yielding radicals **I**, also involves intermediate formation of azo imines **II** [scheme (2)].

The stable radical 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**Ia**), its selectively isotope-substituted analogs, and 1-(4-chlorophenyl) (**Ib**) and 3-*tert*-butyl derivatives were studied previously by ESR [2–6, 11]. In the ESR spectra of benzotriazinyl radicals



(2)

I, the largest hyperfine coupling constant is observed with the N^1 atom of the ring (~7.5 G), whereas the coupling constants with N^2 and N^4 are smaller and unexpectedly equal to each other (~5.1 G). The hyperfine coupling constants with the protons of the N–Ph and C–Ph phenyl rings also differ significantly. These facts were initially attributed to free rotation of the *N*-aryl ring around the N–Ar bond and to presumed considerable contribution of dipolar structure **IV** to the ground state of benzotriazinyl radicals **I**.



IV

To confirm these assumptions, not only spectroscopic but also single-crystal X-ray diffraction studies were made. Neugebauer [4, 11] initially failed to obtain a single crystal of **Ia** of X-ray quality, but solved a structure of a related compound, 1-(4-chlorophenyl)-3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**Ib**). Here we report on a single-crystal X-ray diffraction study of **Ia** (for a preliminary communication, see [13]). The sample of **Ia** prepared in our institute by thermolysis of 1,4-diphenyl-2-benzylidenebenzhydrazidine consists of black prismatic crystals [7]. The crystal used for the X-ray diffraction study was grown from ethanol.

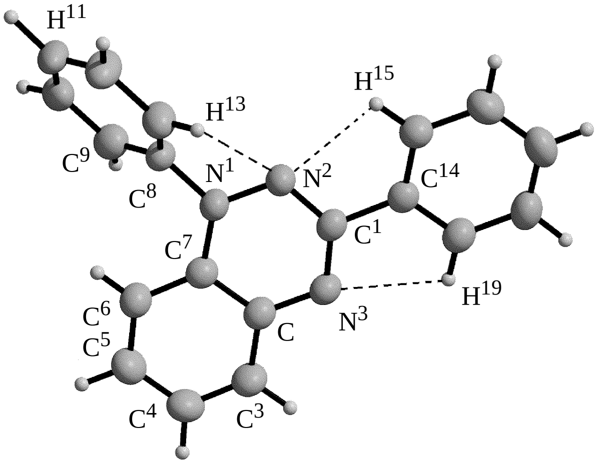


Fig. 1. Geometry of **Ia** in the crystal, with the atom numbering.

The projection of the molecule of **Ia** and the atom numbering are shown in Fig. 1. The atomic coordinates and the selected geometric parameters of the molecule are given in Tables 1 and 2, respectively. In contrast to expectations, the N^1 atom has a trigonal planar configuration unusual for N atoms in $8n\pi$ heterocycles [14, 15] such as 1,4-dihydro-1,2,4-benzotriazine derivatives. The sum of the bond angles at N^1 in **Ia** is 359.7°; hence, the pyramidality parameter $C_p(N^1)$ is 0.01 $\{C_p(N^1) = 9.000 - 0.025\omega N$, where ωN is the sum of the bond angles at the N atom [16]$\}$. In 4-chlorophenyl derivative **Ib**, the N^1 atom has the same configuration (cf. [11]).

The whole dihydrobenzo-1,2,4-triazine moiety is also planar, whereas the majority of heterocycles with the $8n\pi$ electronic system, including 1,2,4-triazine derivatives, have usually the *boat* conformation [14, 15]. The phenyl substituent at C^1 is virtually coplanar with the heteroring plane [the dihedral angle between their planes is 10.5(1)°]. The Ph substituent is turned about the C^1–Ph bond by only 8.0° (as calculated from the four torsion angles, Table 2), i.e., by even a smaller angle than in 4-chlorophenyl analog **Ib** (15.9°) [11]. At the same time, the *N*-phenyl substituent in **Ia**, as also the 4-chlorophenyl substituent in **Ib**, is appreciably turned relative to the heteroring plane. This fact is responsible for the low hyperfine coupling constants with the protons of these rings in the ESR spectra. The calculated torsion angles of these substituents about the N^1–Ph bond are 54.0° in **Ia** and 56.9° in **Ib**.

The C^1–N^2 and C^1–N^3 bond lengths [1.336(2) and 1.333(2) Å] take intermediate values between the typical lengths of single (1.426 Å) and double (1.281 Å) C–N bonds [17], suggesting strong conjugation in the amidine moiety of the heterocycle. The decrease in the $C^1N^2N^1$ and $C^1N^3C^2$ bond angles to ~116° (Table 2), compared to the standard value of 120° for the benzene ring, is typical of azines containing a two-coordinate sp^2-hybridized pyridine nitrogen atom [15, 18].

Among intermolecular interactions revealed in the crystal, we should note interactions of two types: C–H···N and π–π interactions. The hydrogen bonds between H^{11} and $N^{3'}$ $(1 + x, y, z)$ [$H^{11}\cdots N^{3'}$ 2.51(2) Å, $\angle C^{11}$–$H^{11}\cdots N^{3'}$ 173.8(2)°] link the molecules in infinite chains running along the $0x$ crystallographic

Table 1. Coordinates and equivalent isotropic thermal parameters $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å) of atoms in structure **Ia**

Atom	*x*	*y*	*z*	*B*
N^1	0.4731(2)	0.2140(3)	–0.34256(8)	3.37(4)
N^2	0.4409(2)	0.2110(3)	–0.27839(8)	3.36(4)
N^3	0.2165(2)	0.2029(3)	–0.32812(9)	3.37(4)
C^1	0.3145(2)	0.2058(4)	–0.2760(1)	3.07(5)
C^2	0.2507(2)	0.1948(4)	–0.3917(1)	3.21(5)
C^3	0.1545(2)	0.1782(4)	–0.4491(1)	4.04(6)
C^4	0.1859(2)	0.1626(4)	–0.5133(1)	4.32(6)
C^5	0.3146(2)	0.1646(4)	–0.5217(1)	4.36(6)
C^6	0.4117(2)	0.1824(4)	–0.4667(1)	3.83(5)
C^7	0.3806(2)	0.1996(4)	–0.4013(1)	3.20(5)
C^8	0.6092(2)	0.2134(4)	–0.3426(1)	3.41(5)
C^9	0.6635(2)	0.3500(4)	–0.3798(1)	4.24(6)
C^{10}	0.7963(2)	0.3472(5)	–0.3795(1)	5.21(7)
C^{11}	0.8722(2)	0.2132(5)	–0.3423(1)	5.60(8)
C^{12}	0.8177(2)	0.0793(5)	–0.3050(1)	5.56(7)
C^{13}	0.6854(2)	0.0781(5)	–0.3047(1)	4.39(6)
C^{14}	0.2827(2)	0.2039(4)	–0.2057(1)	3.10(5)
C^{15}	0.3778(2)	0.1819(4)	–0.1487(1)	3.90(5)
C^{16}	0.3448(3)	0.1757(4)	–0.0842(1)	4.62(6)
C^{17}	0.2177(3)	0.1916(4)	–0.0754(1)	4.58(6)
C^{18}	0.1239(2)	0.2144(4)	–0.1311(1)	4.53(6)
C^{19}	0.1546(2)	0.2199(4)	–0.1964(1)	3.86(6)
H^3	0.063(2)	0.171(3)	–0.442(1)	5.5(6)[a]
H^4	0.114(2)	0.144(3)	–0.551(1)	4.3(5)[a]
H^5	0.340(2)	0.150(3)	–0.567(1)	5.5(6)[a]
H^6	0.498(2)	0.180(3)	–0.471(1)	4.5(5)[a]
H^9	0.609(2)	0.446(4)	–0.404(1)	5.8(6)[a]
H^{10}	0.834(2)	0.444(4)	–0.408(1)	7.5(7)[a]
H^{11}	0.974(2)	0.217(4)	–0.341(1)	6.7(7)[a]
H^{12}	0.867(2)	–0.017(4)	–0.279(1)	7.5(7)[a]
H^{13}	0.645(2)	–0.014(4)	–0.279(1)	5.6(6)[a]
H^{15}	0.467(2)	0.166(4)	–0.156(1)	5.9(6)[a]
H^{16}	0.410(2)	0.154(3)	–0.046(1)	5.0(6)[a]
H^{17}	0.195(2)	0.199(4)	–0.032(1)	6.1(7)[a]
H^{18}	0.028(2)	0.226(4)	–0.126(1)	5.8(6)[a]
H^{19}	0.087(2)	0.242(3)	–0.238(1)	4.4(5)[a]

[a] The atoms were refined in the isotropic approximation.

Table 2. Selected bond lengths (*d*, Å), bond angles (ω, deg), and torsion angles (τ, deg) in structure **Ia**

Bond	*d*	Bond	*d*
$N^1–N^2$	1.372(1)	$C^2–C^3$	1.398(2)
$N^1–C^7$	1.392(2)	$C^2–C^7$	1.408(2)
$N^1–C^8$	1.427(2)	$C^3–C^4$	1.373(2)
$N^2–C^1$	1.336(2)	$C^4–C^5$	1.387(2)
$N^3–C^1$	1.333(2)	$C^5–C^6$	1.370(2)
$N^3–C^2$	1.369(2)	$C^6–C^7$	1.397(2)
$C^1–C^{14}$	1.489(2)		
Angle	ω	Angle	ω
$N^2N^1C^7$	122.2(1)	$N^1C^7C^2$	116.4(1)
$N^2N^1C^8$	113.6(1)	$N^1C^7C^6$	123.3(1)
$C^7N^1C^8$	123.9(1)	$C^2C^7C^6$	120.3(1)
$N^1N^2C^1$	115.6(1)	$N^1C^8C^9$	119.9(1)
$C^1N^3C^2$	115.5(1)	$C^2C^3C^4$	120.9(1)
$N^2C^1N^3$	128.0(1)	$C^3C^4C^5$	119.9(1)
$N^2C^1C^{14}$	114.3(1)	$C^4C^5C^6$	121.1(1)
$N^3C^1C^{14}$	117.7(1)	$C^5C^6C^7$	119.5(1)
$N^3C^2C^3$	119.5(1)	$C^1C^{14}C^{15}$	121.6(1)
$N^3C^2C^7$	122.1(1)	$C^3C^2C^7$	118.4(1)
Angle	τ	Angle	τ
$C^7N^1N^2C^1$	–4.1(3)	$C^2C^3C^4C^5$	–0.5(4)
$C^8N^1N^2C^1$	–178.2(2)	$C^3C^4C^5C^6$	–0.1(4)
$N^2N^1C^7C^2$	4.2(3)	$C^4C^5C^6C^7$	–0.3(4)
$N^2N^1C^7C^6$	–173.2(2)	$C^5C^6C^7N^1$	178.6(3)
$C^8N^1C^7C^2$	177.6(2)	$C^5C^6C^7C^2$	1.3(4)
$C^8N^1C^7C^6$	0.2(4)	$N^3C^2C^3C^4$	–177.6(2)
$N^2N^1C^8C^{13}$	50.6(3)	$C^7C^2C^3C^4$	1.4(4)
$C^7N^1C^8C^9$	57.7(3)	$N^3C^2C^7N^1$	–0.3(3)
$N^1N^2C^1N^3$	0.1(3)	$N^3C^2C^7C^6$	177.1(2)
$N^1N^2C^1C^{14}$	–179.6(2)	$C^3C^2C^7N^1$	–179.3(2)
$C^2N^3C^1N^2$	3.5(4)	$C^3C^2C^7C^6$	–1.8(4)
$C^2N^3C^1C^{14}$	–176.8(2)	$N^2C^1C^{14}C^{19}$	172.9(2)
$C^1N^3C^2C^3$	175.7(2)	$N^3C^1C^{14}C^{15}$	171.6(2)
$C^1N^3C^2C^7$	–3.2(4)		

axis (Fig. 2). Interactions of the electronic systems of the bicyclic moiety and phenyl substituents of the molecules related to the initial molecule by $(3/2 - x, 1/2 + y, 1/2 - x)$ and $(3/2 - x, -1/2 + y, 1/2 - z)$ cause stacking of the molecules along the 0*y* axis. The shortest distance between the ring planes is 3.38(2) Å, and the dihedral angle is 4.4(2)°.

The combined effect of the two types of intermolecular contacts causes formation of a lamellar supramolecular structure; the molecular layers are arranged parallel to the 0*ab* plane (Fig. 3). Along with these contacts, there are intramolecular contacts of the phenyl protons H^{15} and H^{19} with the N^2 and N^3 atoms of the bicyclic moiety [distances 2.43(2) and 2.44(2) Å, respectively], stabilizing the coplanar arrangement of one of the phenyl substituents relative to the heteroring.

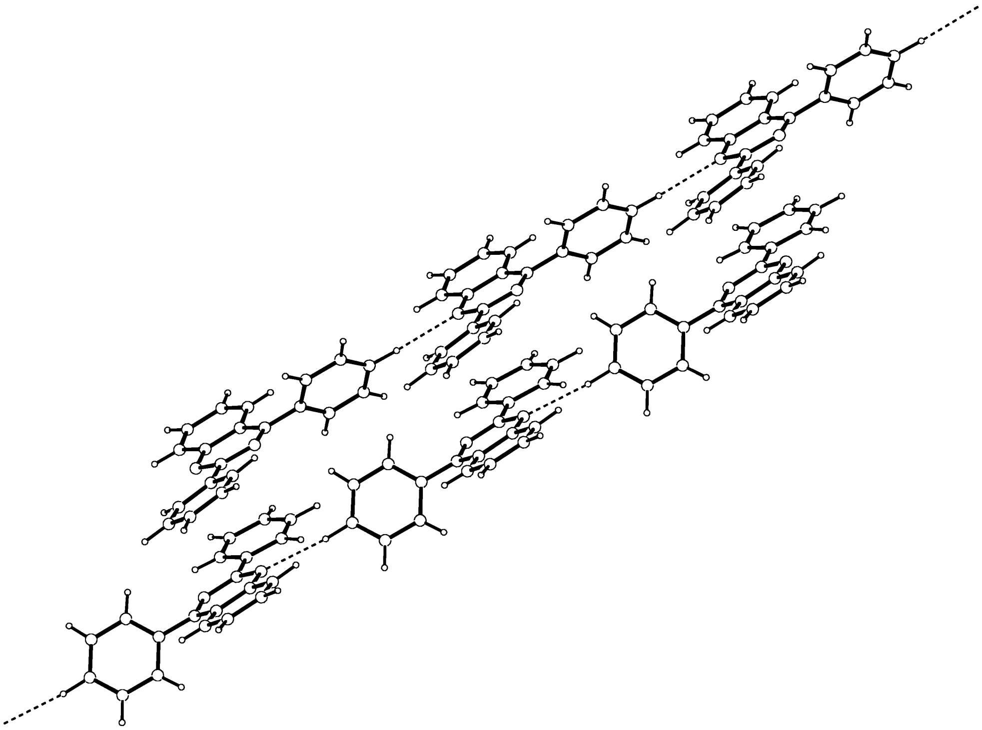


Fig. 2. Formation of infinite chains of hydrogen-bonded molecules in the crystal of **Ia** (hydrogen bonds are shown with dashed lines).

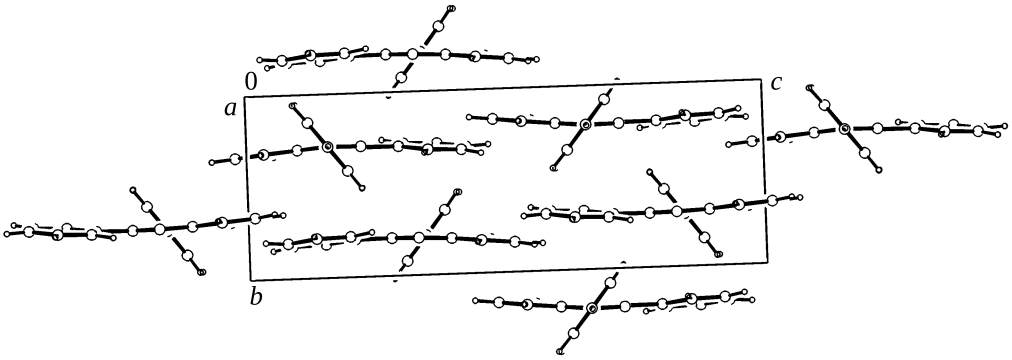
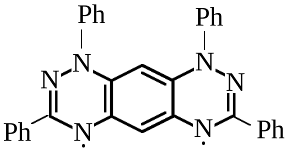


Fig. 3. Molecular packing in the crystal of **Ia** (view along 0*a* axis).

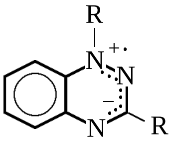
Note that the second phenyl substituent does not participate in the π–π contacts, but its position relative to the plane of the bicyclic moiety is stabilized by weak interactions C–H···π and C–H···N, e.g., between H^{12} and $N^{2'}$ (1/2 – *x*, 1/2 + *y*, 1/2 – *z*) with the parameters $H^{12}\cdots N^{2'}$ 2.85(2) Å, $\angle C^{12}–H^{12}\cdots N^{2'}$ 130.1(5)°. There is also an intramolecular contact between the H^{13} atom of the phenyl ring and the N^2 atom of the heteroring [distance 2.65(2) Å]. Further turn of the phenyl ring toward the heteroring plane is probably prevented by steric interactions, since even at this position the distance between the C^6 and C^9 atoms [3.133(2) Å] is appreciably shorter than the sum of their van der Waals radii (3.40 Å).

Such molecular packing in the crystal, despite deviation of one of the phenyl rings from planarity, results in a fairly high packing coefficient (70.2%) and absence of voids potentially accessible for solvent molecules. This lamellar supramolecular structure should, apparently, be manifested in anisotropy of certain physical properties.

Our results in combination with published data, including those for bistriazinyl “biradical” **V** [12], allow a substantiated conclusion that the extremely high stability of 1,4-dihydro-1,2,4-benzotriazin-4-yl radicals **I** is due to the high degree of delocalization of the unpaired electron, preferably in the amidrazone moiety of the dihydro-1,2,4-benzotriazinyl ring, irrespective of substituents in the 1-phenyl group [2–6, 11–13]. Taking into account the ESR data, the structure of these compounds can be described by formula **VI**, similar to formula **IV** suggested previously [2, 4] as one of the possible resonance structures of these radicals.



V



VI

EXPERIMENTAL

The free radical 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**Ia**) was prepared as described in [7].

Single-crystal X-ray diffraction study of Ia was performed with an Enraf-Nonius CAD-4 automatic fourcircle diffractometer. The crystals of **Ia**, $C_{19}H_{14}N_3$, are monoclinic. At 20°C, *a* 10.492(2), *b* 6.959(6), *c* 19.864(2) Å; β 99.51(5)°, *V* 1430.5(4) $Å^3$, *Z* 4, d_{calc} 1.32 g cm^{-3}, space group $P2_1/n$. The unit cell parameters and the intensities of 3343 reflections, including 1544 reflections with $I \geq 3\sigma$, were measured at 20°C (λCu $K_\alpha$radiation, graphite monochromator, ω/2θ scanning, $\theta \leq 74.23°$). The intensities of three check reflections did not decrease in the course of the measurements. The absorption was taken into account empirically (μ 5.89 cm^{-1}). The structure was solved by the direct method using the SIR program [19] and refined first in the isotropic and then in the anisotropic approximation. All hydrogen atoms were subsequently revealed from the difference electron density series and refined in the isotropic approximation. The final divergence factors were *R* 0.047 and R_W 0.057 for 1544 unique reflections with $F^2 \geq 3\sigma$. All the calculations were performed on an AlphaStation 200 computer using the MolEN software [20]. The figures were plotted and the intermolecular interactions calculated using the PLATON program [21].

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