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# 6,7-Diphenyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazine

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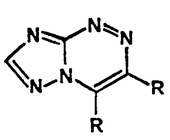
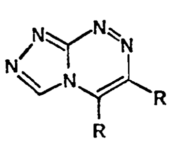
**Abstract.** $C_{16}H_{11}N_5$, $M_r = 273\cdot304$, monoclinic, $P2_1/n$, $a = 12\cdot846$ (11), $b = 7\cdot664$ (7), $c = 13\cdot610$ (12) Å, $\beta = 92\cdot58$ (6)°, $Z = 4$, $V = 1338\cdot56$ Å$^3$, $D_c = 1\cdot36$, $D_m = 1\cdot33$ g cm$^{-3}$ (flotation). Direct phase determination and constrained full-matrix least-squares refinement reduced $R$ to 0·072. The bicyclic system shows extensive delocalization, and is flat within ±0·03 Å. The phenyl rings are inclined to it at angles of 56·2 and 50·8°, and bent away from each other to reduce crowding.

**Introduction.** Interaction of 3-hydrazino-1,2,4-triazole and 1,2-diketones can afford entry to either the [1,2,4]-triazolo[5,1-*c*][1,2,4]triazine ring system (I*a*) or the isomeric [1,2,4]triazolo[3,4-*c*][1,2,4]triazine series (I*b*) (Gray & Stevens, 1976).



(I*a*)



(I*b*)

Since type (I*b*) 1,2,4-triazoloazines undergo Dimroth rearrangement to type (I*a*) (Daunis, Jacquier & Viallefont, 1969), fusion as in (I*a*) appears thermodynamically more stable in agreement with CNDO calculations (Guerret, Jacquier & Maury, 1971). A case in point is the triazolotriazine formed by reacting 3-hydrazino-1,2,4-triazole and benzil, which was assigned structure (I*a*) ($R$ = Ph) on the scant evidence of the chemical shift of the triazole proton and the lack of rearrangement in acid or base (Gray & Stevens, 1976). We undertook a crystal structure determination to verify this assignment and investigate the stereochemical relationship of the rings.

Crystals of the title compound exhibited systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicating space group $P2_1/n$. From a crystal 0·58 × 0·46 × 0·12 mm mounted along $b$, 2540 reflexions were collected on a STADI-2 two-circle diffractometer (Mo $K\alpha$, $\mu = 0\cdot0920$ mm$^{-1}$). Another crystal 0·72 × 0·24 × 0·20 mm mounted along [$\bar{1}01$] was used for multiple-film Weissenberg photographs (Cu $K\alpha$, $\mu = 0\cdot689$ mm$^{-1}$). Evaluation by microdensitometer of levels 0 to 4 yielded 411 reflexions. Upon merging of diffractometer and film data the $R$ factor for 2475 unique data was 6·8%. This value of $R$ was

$$\left(\left\{\sum_{hkl} n \sum_{i=1}^{n} w_i[\bar{F}(hkl) - F_i(hkl)]^2\right\} \Bigg/ \left[\sum_{hkl} (n-1) \sum_{i=1}^{n} w_i F_i(hkl)^2\right]\right)^{1/2}$$

where the outer summations are over all unique $hkl$, each inner summation is over the $n$ multiple observations, $\bar{F}(hkl)$ is the mean of these, and $F_i(hkl)$ and $w_i$ are the individual observations and their weights. After elimination of reflexions with $F < 4\sigma(F)$ as well as three

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intense low-angle reflexions, 1739 independent observations were carried forward.

The structure was determined by direct methods. From a subsequently discarded set of very crude film data the *XCSD* system (Sheldrick, 1975*a*) on an Eclipse computer produced the molecule, but shifted from its correct position by a prominent Patterson vector. With the full data set *MULTAN* (Germain, Main & Woolfson, 1971) revealed the correct location. Least-squares refinement of positions and isotropic temperature factors was carried out with C atom scattering factors for all atoms. N atoms could be distinguished by $B$ values 0·5–1·0 Å$^2$ lower than those for C atoms in similar surroundings. Structure (I*a*) is confirmed.

Final least-squares refinement was performed by the *SHELX* system (Sheldrick, 1975*b*) with benzene rings constrained to be regular hexagons of side 1·395 Å and H atoms assumed to ride on their attached atom. The weighting function was $1/[\sigma^2(F) + KF^2]$ with $K$ a refinable parameter that converged to 0·003. After final refinement including anisotropic thermal parameters for non-hydrogen atoms and a common isotropic temperature factor for hydrogens (converging to $B = 6{\cdot}25$ Å$^2$), $R = 0{\cdot}072$ and $R_w = 0{\cdot}079$. A difference electron density map showed no feature greater than ±0·25 e Å$^{-3}$. Atomic coordinates are listed in Table 1.*

**Discussion.** The C(9) and C(15) phenyl rings are disposed about the heterocycle like blades on a propeller shaft (Fig. 1). Their planes intersect at 62·5° and intersect the plane of the flat (to ±0·03 Å) heterocycle at 56·2 and 50·8° respectively. Other examples of benzene rings on adjacent $sp^2$ C atoms occur in *cis,cis*-1,2,3,4-tetraphenylbutadiene (Karle & Dragonette, 1965) with 75 and 34° inclination of rings to chain, and 4,5,6-tris(*p*-methoxyphenyl)-1,2,3-triazine (Oeser & Schiele, 1972) with 37, 68 and 37° inclination of benzene rings to triazine. In the title compound (I*a*) a twist of 8·6° about C(6)–C(7) prevents eclipse of C(9) and C(15) and reduces steric hindrance between phenyl rings; even so, the shortest C–C contact is 3·073 Å.

Bond distances (Table 2) and angles (Table 3) in the triazine unit may be compared with those in 5-*p*-chlorophenyl-1,2,4-triazine (II) (Atwood, Krass & Paudler, 1974). Steric hindrance is apparently not relieved by stretching C(6)–C(7): this length is 1·386 Å in (I*a*) but 1·401 Å in (II). Some relief is indicated by C(7)–C(6)–C(9) and C(6)–C(7)–C(15) angles well above 120°, showing phenyl substituents spread apart. The triazole moiety is generally similar to 1,2,4-triazole

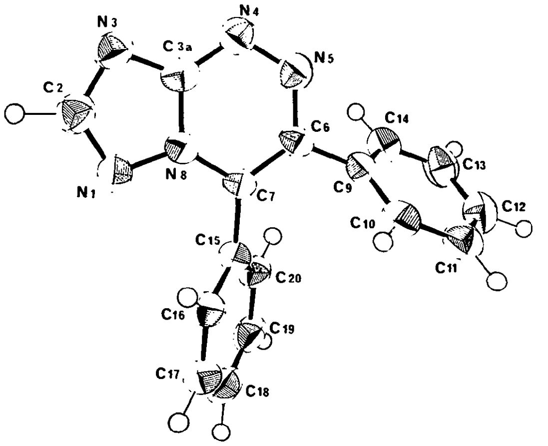

Fig. 1. View of the molecule showing numbering scheme and thermal ellipsoids.

Table 1. *Atomic coordinates in fractions of a unit-cell edge* (× $10^4$)

(*a*) Heterocyclic non-hydrogen atoms with standard deviations

| | *x* | *y* | *z* |
|---|---|---|---|
| N(1) | −96 (2) | 7814 (4) | −38 (2) |
| C(2) | −1044 (3) | 7529 (5) | 283 (3) |
| N(3) | −1119 (3) | 6487 (4) | 1069 (2) |
| C(3a) | −120 (3) | 6093 (5) | 1280 (3) |
| N(4) | 267 (2) | 5115 (4) | 2022 (2) |
| N(5) | 1289 (3) | 4918 (4) | 2092 (2) |
| C(6) | 1928 (3) | 5683 (4) | 1443 (2) |
| C(7) | 1565 (2) | 6753 (4) | 681 (2) |
| N(8) | 506 (2) | 6871 (3) | 611 (2) |

(*b*) Phenyl carbon positions from rigid-group refinement

| | *x* | *y* | *z* |
|---|---|---|---|
| C(9) | 3052 | 5251 | 1618 |
| C(10) | 3614 | 4473 | 882 |
| C(11) | 4657 | 4024 | 1066 |
| C(12) | 5138 | 4353 | 1987 |
| C(13) | 4576 | 5131 | 2723 |
| C(14) | 3533 | 5580 | 2539 |
| C(15) | 2201 | 7788 | 28 |
| C(16) | 2014 | 7793 | −990 |
| C(17) | 2619 | 8833 | −1583 |
| C(18) | 3412 | 9868 | −1158 |
| C(19) | 3599 | 9863 | −140 |
| C(20) | 2994 | 8823 | 453 |

Table 2. *Bond distances* (Å) *with estimated standard deviations in parentheses*

| | | | |
|---|---|---|---|
| N(1)–C(2) | 1·330 (5) | N(4)–N(5) | 1·320 (4) |
| C(2)–N(3) | 1·342 (5) | N(5)–C(6) | 1·366 (5) |
| N(3)–C(3a) | 1·336 (5) | C(6)–C(7) | 1·386 (5) |
| C(3a)–N(8) | 1·379 (5) | C(7)–N(8) | 1·363 (4) |
| N(8)–N(1) | 1·356 (4) | C(6)–C(9) | 1·490 (4) |
| C(3a)–N(4) | 1·335 (5) | C(7)–C(15) | 1·468 (4) |

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* Lists of observed and calculated structure factors, and tables of anisotropic thermal parameters, hydrogen positions, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33708 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles (°) with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| N(8)–N(1)–C(2) | 101·7 (3) | N(1)–N(8)–C(7) | 128·3 (3) |
| N(1)–C(2)–N(3) | 117·3 (4) | N(3)–C(3a)–N(4) | 127·7 (4) |
| C(2)–N(3)–C(3a) | 101·8 (3) | N(5)–C(6)–C(9) | 114·1 (3) |
| N(3)–C(3a)–N(8) | 110·0 (3) | C(7)–C(6)–C(9) | 122·8 (3) |
| C(3a)–N(8)–N(1) | 109·2 (3) | C(6)–C(7)–C(15) | 126·5 (3) |
| N(4)–C(3a)–N(8) | 122·2 (3) | N(8)–C(7)–C(15) | 120·2 (3) |
| C(3a)–N(4)–N(5) | 117·0 (3) | C(6)–C(9)–C(10) | 120·6 (2) |
| N(4)–N(5)–C(6) | 122·0 (3) | C(6)–C(9)–C(14) | 119·4 (2) |
| N(5)–C(6)–C(7) | 123·1 (3) | C(7)–C(15)–C(16) | 121·8 (2) |
| C(6)–C(7)–N(8) | 113·1 (3) | C(7)–C(15)–C(20) | 118·2 (2) |
| C(7)–N(8)–C(3a) | 122·4 (3) | | |

itself (III) (Goldstein, Ladell & Abowitz, 1969). However, the bridge bond C(3a)–N(8) in (I*a*) at 1·379 Å is considerably longer than in either single ring [1·339 Å in (II), 1·326 Å in (III)], and the opposite angle N(1)–C(2)–N(3) is correspondingly 2·7° larger in (I*a*) than in (III). All ring bonds are intermediate between single and double.

The packing of molecules in the unit cell is illustrated in Fig. 2. The $\pi$-deficient triazine portion of the heterocycle is covered by a phenyl ring from a neighbouring molecule at ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) with contacts N(8)···C(13′) 3·379 Å and C(3a)···C(12′) 3·437 Å. However, the least-squares planes of the two rings are not parallel but intersect at 25·6°. Other intermolecular contacts are normal throughout.

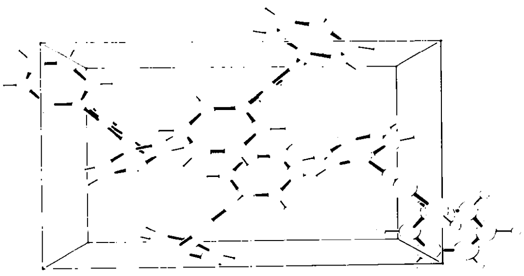

Fig. 2. Projection of the unit-cell contents along *a*.

We thank Dr T. A. Hamor for diffractometer facilities and the 3M Company for a research studentship (to EJG). Most computations were carried out at the University of Aston Computer Centre, the University of Manchester Regional Computer Centre, and the Atlas Computer Laboratory. The initial direct methods work was kindly done by Dr G. M. Sheldrick.

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# A Toxaphene Component: 2,5,6-*exo*,8,8,9,10-Heptachlorodihydrocamphene

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**Abstract.** $C_{10}H_{11}Cl_7$, triclinic, $P\bar{1}$, $a = 8{\cdot}745\,(1)$, $b = 11{\cdot}156\,(1)$, $c = 7{\cdot}942\,(5)$ Å, $\alpha = 99{\cdot}83\,(3)$, $\beta = 114{\cdot}64\,(3)$, $\gamma = 85{\cdot}16\,(3)°$, $Z = 2$, $D_m$ (room temperature) = 1·76, $D_x$ (85 K) = 1·81 g cm$^{-3}$. The structure was determined from diffractometer data (Mo $K\alpha$) measured at 85 K, and refined (anisotropic $B$'s for