

that this product was not formed, but instead the isomer, 3,3'-dimethyl-5,5'-diphenyl-4,4'-bi-4H-1,2,4-triazole, **4**. These results clearly indicated that the product was not formed by a simple addition–ring closure reaction.

Structure of 4. The conformational properties of bitriazoles are of special interest, particularly those substituted with sterically more demanding groups. Molecular structures of bitriazoles have been reported before⁶ and also for a series of metal complexes of the parent bitriazole.⁷

Crystal structure analysis: crystal data. C₁₈H₁₆N₆, *M_r* = 316.4, monoclinic space group, *P*2₁/*n*, *a* = 9.072(6), *b* = 11.393(12), *c* = 15.698(3) Å, β = 96.60(3)°, *V* = 1612(2) Å³, *Z* = 4, *D*_{calc} = 1.30 g cm⁻³, μ(MoK_α) = 0.77 cm⁻¹. A crystal with the approximate dimensions 0.30 × 0.30 × 0.30 mm was mounted on a glass fibre. Diffracted intensities (+*h*, +*k*, ±*l*) were measured, for 3.5° < 2θ < 50°, at -150°C, using graphite-monochromated MoK_α radiation and a Rigaku AFC6R diffractometer, equipped with a 12 kW rotating anode generator. The ω/2θ scan mode was employed with an ω scan rate of 8' min⁻¹ and a scan width of (1.57 + 0.30 tanθ)°. Weak reflections [*I* < 10σ(*I*)] were rescanned twice and counts accumulated to improve the counting statistics. Stationary background counts were recorded on each side of the reflections. The ratio of peak counting time vs. background-counting time was 2:1. Of the 2972 independent reflections measured, 1686 had *I* > 3σ(*I*) and were regarded as being observed. That the crystal was not subject to decay during the measurement of intensities was checked by monitoring three reflections at regular intervals (after measurement of 150 reflections).

Table 1. Crystal data and structure parameters of compound **4**.

Compound	C ₁₈ H ₁₆ N ₆
Diffractometer	Rigaku AFC6R
Radiation, wavelength/Å	MoK _α , 0.71069
Crystal system	Monoclinic
<i>a</i> /Å	9.072(6)
<i>b</i> /Å	11.393(12)
<i>c</i> /Å	15.698(3)
β/°	96.60(3)°
<i>V</i> /Å ³	1612(2)
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>M_r</i>	316.4
<i>Z</i>	4
<i>D</i> _{calc} /g cm ⁻³	1.30
μ(MoK _α)/cm ⁻¹	0.77
Crystal dimensions/mm	0.30 × 0.30 × 0.30
<i>T</i> (data collection)/K	123
2θ range/°	3.5 < 2θ < 50
2θ scan rate/° min ⁻¹	8
Scan mode	ω/2θ
No. of independent measurements	2972
<i>I</i> > 3σ(<i>I</i>)	1686
<i>R</i>	0.050
<i>R_w</i>	0.054
Correction for absorption	None
Max., min. residual electron density/e Å ⁻³	+0.31; -0.33

Intensity data were corrected for Lorentz and polarization effects, but no correction was made for the effects of absorption. Unit-cell parameters were obtained from diffractometer setting angles for 25 reflections in the range 22.3° < 2θ < 34.9° (Table 1).

Structure determination and refinement. The structure was solved by direct methods (MITHRIL).⁸ Full-matrix least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms gave the final values *R* = 0.050, *R_w* = 0.054 for 217 parameters and 1686 reflections, hydrogen atoms being included as a fixed contribution in calculated positions C–H = 0.95 Å, *B* = 1.2**B*_{eq} of the carrying carbon atom. Atomic scattering factors were taken from Ref. 9, and the *F_o* values were weighted according to *w* = [σ²(*F_o*)]⁻¹. All calculations were carried out with the TEXSAN program system.¹⁰

Results and discussion

The molecular structure of **4** is illustrated in Fig. 1. The bond lengths (Å) and angles (°) in the molecule were calculated from the coordinates given in Table 2 and listed in Tables 3 and 4, together with standard deviations. The interatomic distances within the rings are very similar to those found in phenyl-substituted triazoles,² except for the N–N distance, e.g. N(3)–N(4), 1.423 Å, which is noticeably longer, almost equivalent to a single bond. This appears to be a characteristic feature of bitriazoles. Similar long triazole N–N bonds has been observed in metal complexes of the parent bitriazole.⁷ The bond length of the linking N–N' bond (1.384 Å) is somewhat shorter than the N–N single bond. Accepted values of N–N single and double bonds, respectively, are 1.451(5) Å and 1.25(2) Å.¹¹ This indicates some attraction between the heterocyclic rings although they are not fully conjugated systems. This finding is also as expected for the twisted bitriazole structure. The triazole rings are close to being perpendicular with a dihedral angle of 73°. Furthermore, the C–C bonds between the phenyl

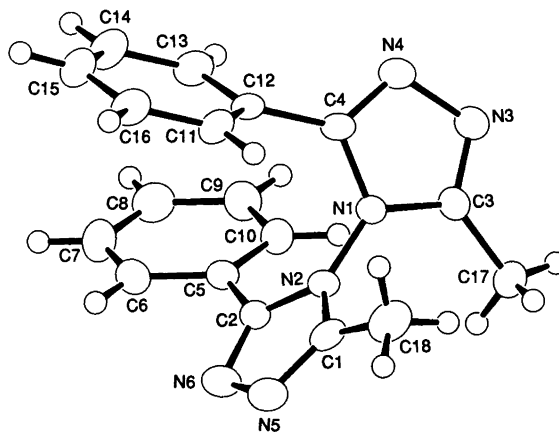


Fig. 1. View of the molecular structure of **4**.

Table 2. Fractional atomic parameters for the non-hydrogen atoms with estimated standard deviations in parentheses.

Atoms	x	y	z	B_{eq}^a
N(1)	0.9194(3)	0.2880(2)	0.3944(2)	1.8(1)
N(2)	0.9881(3)	0.1796(2)	0.3945(2)	2.0(1)
N(3)	0.8417(3)	0.4559(2)	0.4383(2)	2.4(1)
N(4)	0.8840(3)	0.4615(2)	0.3480(2)	2.4(1)
N(5)	1.0173(4)	-0.0103(3)	0.3899(2)	3.0(1)
N(6)	1.1519(3)	0.0446(2)	0.3764(2)	2.9(1)
C(1)	0.9218(4)	0.0726(3)	0.3996(2)	2.4(2)
C(2)	1.1332(4)	0.1579(3)	0.3789(2)	2.1(1)
C(3)	0.8883(3)	0.3524(3)	0.4639(2)	2.0(1)
C(4)	0.8915(3)	0.3604(3)	0.3235(2)	1.8(1)
C(5)	1.2420(4)	0.2483(3)	0.3619(2)	2.2(1)
C(6)	1.3390(4)	0.2223(3)	0.3023(2)	2.9(2)
C(7)	1.4442(4)	0.3035(4)	0.2840(2)	3.4(2)
C(8)	1.4536(4)	0.4111(4)	0.3251(2)	3.3(2)
C(9)	1.3577(4)	0.4375(3)	0.3848(2)	2.7(2)
C(10)	1.2519(4)	0.3568(3)	0.4027(2)	2.4(1)
C(11)	0.8518(4)	0.2299(3)	0.1952(2)	2.2(1)
C(12)	0.9215(3)	0.3263(3)	0.2368(2)	1.8(1)
C(13)	1.0231(4)	0.3908(3)	0.1973(2)	2.4(2)
C(14)	1.0546(4)	0.3602(3)	0.1159(2)	2.8(2)
C(15)	0.9831(4)	0.2659(3)	0.0741(2)	2.7(2)
C(16)	0.8835(4)	0.1997(3)	0.1137(2)	2.5(1)
C(17)	0.9127(4)	0.3086(3)	0.5533(2)	2.6(1)
C(18)	0.7637(4)	0.0565(3)	0.4124(2)	3.4(2)

^a B_{eq} is defined as $(8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

rings and the heterocycles are long, 1.470 and 1.472 Å, indicating reduced conjugation. The phenyl rings are also twisted out of plane with the heterocyclic rings, exhibiting angles of 60 and 35°, respectively. Angles were determined between least-squares planes.

The stereo structure of the molecule, Fig. 2, is noteworthy. Each molecule has a clip-like shape with the phenyl groups as the jaws and the linked triazole groups as the hinges. This may give the material two interesting properties, which we plan to investigate further: (a) the ability to form complexes with molecules such as I_2 , where I_2 could occupy the space between the jaws, or possibly even com-

Table 3. Selected interatomic distances (in Å) and angles (in degrees). Estimated standard deviations in the least significant figure are given in parentheses.

Atom	Atom	Distance	Atom	Atom	Distance
N(1)	N(2)	1.384(4)	C(4)	C(12)	1.470(4)
N(1)	C(3)	1.371(4)	C(5)	C(6)	1.388(5)
N(1)	C(4)	1.384(4)	C(5)	C(10)	1.390(5)
N(2)	C(1)	1.366(4)	C(6)	C(7)	1.382(5)
N(2)	C(2)	1.388(4)	C(7)	C(8)	1.384(5)
N(3)	N(4)	1.423(4)	C(8)	C(9)	1.383(5)
N(3)	C(3)	1.301(4)	C(9)	C(10)	1.382(5)
N(4)	C(4)	1.304(4)	C(11)	C(12)	1.392(4)
N(5)	N(6)	1.409(4)	C(11)	C(16)	1.387(4)
N(5)	C(1)	1.302(4)	C(12)	C(13)	1.380(4)
N(6)	C(2)	1.304(4)	C(13)	C(14)	1.386(5)
C(1)	C(18)	1.482(5)	C(14)	C(15)	1.381(5)
C(2)	C(5)	1.472(5)	C(15)	C(16)	1.379(5)
C(3)	C(17)	1.482(5)			

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N(2)	N(1)	C(3)	127.6(3)	N(1)	C(3)	C(17)	123.5(3)
N(2)	N(1)	C(4)	125.0(3)	N(3)	C(3)	C(17)	127.2(3)
C(3)	N(1)	C(4)	106.6(3)	N(1)	C(4)	N(4)	109.0(3)
N(1)	N(2)	C(1)	126.6(3)	N(1)	C(4)	C(12)	123.4(3)
N(1)	N(2)	C(2)	126.5(3)	N(4)	C(4)	C(12)	127.5(3)
C(1)	N(2)	C(2)	106.5(3)	C(2)	C(5)	C(6)	117.6(3)
N(4)	N(3)	C(3)	107.9(3)	C(2)	C(5)	C(10)	123.1(3)
N(3)	N(4)	C(4)	107.3(3)	C(6)	C(5)	C(10)	119.2(3)
N(6)	N(5)	C(1)	107.2(3)	C(5)	C(6)	C(7)	120.2(3)
N(2)	C(1)	N(5)	109.7(3)	C(7)	C(8)	C(9)	119.9(4)
N(2)	C(1)	C(18)	123.9(3)	C(8)	C(9)	C(20)	120.0(3)
N(5)	C(1)	C(18)	126.4(3)	C(4)	C(12)	C(11)	121.4(3)
N(2)	C(2)	N(6)	108.1(3)	C(4)	C(12)	C(13)	118.7(3)
N(2)	C(2)	C(5)	125.3(3)	C(11)	C(12)	C(13)	120.0(3)
N(6)	C(2)	C(5)	126.5(3)	C(12)	C(13)	C(14)	120.0(3)
N(1)	C(3)	N(3)	109.2(3)	C(13)	C(14)	C(15)	199.9(3)

plexation with a suitable transition metal and (b) elastic anisotropy implying hinge deformation under non-axial stress. This effect could in fact be retained in the solid phase, because the molecules have a preferred orientation relative to the glide plane [101].

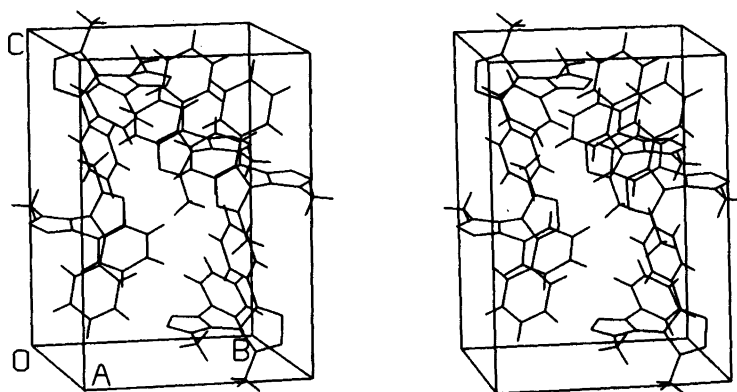


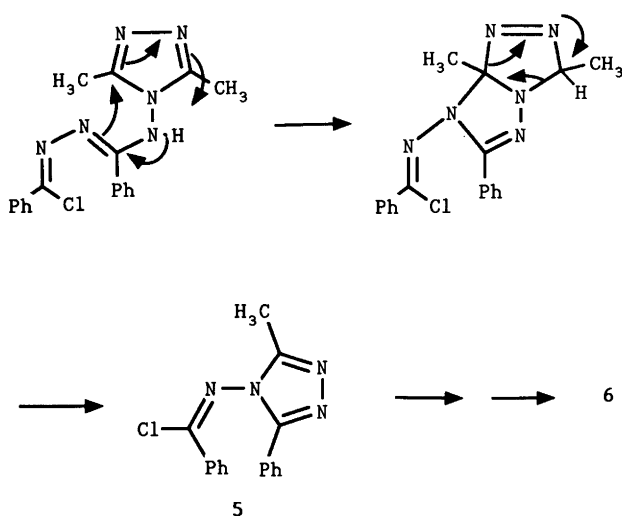
Fig. 2. A stereoscopic drawing of the unit-cell packing.

Table 4. Selected torsion angles (in degrees) with estimated standard deviations in parentheses. The sign is positive if when looking from atom 2 to 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Bond	Angle
N(1) N(2) C(1) N(5)	174.1(3)
N(1) N(2) C(1) C(18)	-4.7(5)
N(1) N(2) C(2) N(6)	-173.9(3)
N(1) N(2) C(2) C(5)	1.9(5)
N(1) C(4) C(12) C(11)	60.8(4)
N(1) C(4) C(12) C(13)	-118.0(3)
N(2) N(1) C(3) N(3)	171.5(3)
N(2) C(2) C(5) C(10)	37.5(5)
N(6) C(2) C(5) C(6)	32.2(5)
C(1) N(2) N(1) C(3)	84.1(4)
C(2) N(2) N(1) C(4)	64.2(4)

Synthesis and properties of 4. The formation of 3,3'-dimethyl-5,5'-diphenyl-4,4'-bi-4H-1,2,4-triazole, **4**, from the reaction of **2** with **3** indicates that the reaction does not proceed via a simple addition–ring closure mechanism. We propose here a mechanism, Scheme 2, for the product formation. An initial nucleophilic displacement of chlorine in **3** by the amino group of **2** followed by an intramolecular ring closure and subsequent elimination of diazoethane results in the intermediate **5**, and a repetition of this reaction sequence at the other imidoil chloride centre gives rise to the product, **4**. However, a rearrangement of an initial ring-closure product cannot be excluded. In support of the proposed mechanism we have detected minor amounts of ethyl benzoate by GLC, when the reaction was performed in the presence of benzoic acid.

The observed spectroscopic data are compatible with both of the bitriazole isomers. Thus, in the proton NMR of the isolated product, **4**, the chemical shift for the methyl groups, δ 2.36 are in good agreement with the value observed for compound **2**, δ 2.25. The shift values for the



Scheme 2.

phenyl groups of **4**, δ 7.3–7.5 (m) deviate from those of 4-amino-3,5-diphenyl-4H-1,2,4-triazole, **3**, δ 8.0 (m, *ortho*) and 7.5 (m, *meta*, *para*). However, this can be explained by conformational differences. We have previously noted that the aromatic proton signals collapses to a broad singlet, when the phenyl groups for steric reasons are twisted out of plane with the triazole ring.

Likewise, carbon-13 NMR spectroscopy did not prove effective to distinguish between the isomers. The methyl signal of **4** observed at δ 9.5 corresponded well with the methyl shift of triazole **2**, δ 9.8, and the phenyl and triazole signals were also in reasonable agreement with those observed for e.g. 4-amino-3,5-diphenyl-4H-1,2,4-triazole (δ 129.8, 129.4, 128.6, 127.3, 151 and 151). The minor differences observed may be attributed to conformational differences. Initially, mass spectrometry appeared to be the best means of detecting the presence of structure **4**, since the cleavage of the N–N bond between the triazole rings represents a characteristic fragmentation.¹² In the mass spectrum of the product a peak of low intensity was observed at m/z 159. However, a peak at m/z 221, that seemed to indicate the presence of structure **4**, was also recorded.

In conclusion, neither NMR nor mass spectrometry were reliable tools in this case to distinguish between the possible isomers. X-Ray structure analysis therefore proved to be the only method for full elucidation of the structure.

Experimental

General. ¹H and ¹³C NMR spectra were recorded on a JEOL-FX-100 NMR spectrometer using DMSO-*d*₆ as the solvent and tetramethylsilane (TMS) as the internal standard. IR spectra were obtained on a NICOLET 20 SXC FT-IR spectrometer, and mass spectra were recorded on an AEI MS-902 double-focusing spectrometer. Melting points are uncorrected.

3,3'-Dimethyl-5,5'-diphenyl-4,4'-bi-4H-1,2,4-triazole, 4. A mixture containing 0.22 g (2.5 mmol) of 4-amino-3,5-dimethyl-4H-1,2,4-triazole, **2**, and 0.70 g (2.5 mmol) of bis(α -chlorobenzylidene)hydrazine, **3**, dissolved in 5 ml of dry xylene was refluxed for 72 h. The reaction mixture was then worked up by washing with 0.1 M HCl, 0.1 M NaOH solution and water and drying over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. Flash chromatography, (silica gel and 15% acetone–hexane) yielded 0.32 g 1.01 mmol, 40%, of the pure product as colourless crystals of m.p. 225–227°C.

Crystals for X-ray structure analysis were grown from a solution of the product in chloroform by slow evaporation of the solvent. The product exhibited the following spectroscopic properties. ¹H NMR (100 MHz): δ 2.36 (s, 6 H), 7.3–7.5 (m, 10 H). ¹³C NMR (25 MHz): δ 9.5, 124.1, 126.3, 129.5, 131.2, 151.0 and 151.5. IR (KBr): 3064, 2922, 2852, 1557, 1542, 1498, 1471, 1442, 1354, 1305, 1182, 1075, 1027,

773, 716, 694, 653, 605 cm^{-1} . MS [m/z (% rel. int.)]: 316 (100, M^+), 246 (2), 221 (3), 159 (2), 144 (3), 129 (4), 118 (6), 117 (6), 104 (9), 103 (39), 89 (25), 77 (6), 76 (6). Found: M^+ 316.1442. Calc. for $\text{C}_{18}\text{H}_{16}\text{N}_6$: M 316.1436.

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