discrepancy could arise because the π interaction in the *d* bonds is actually stronger than calculated, although the agreement for *b* in $C_{12}H_8$ and $C_{12}Me_8$ is excellent. Alternatively (Randić & Maksić, 1971), the 'shortness' of the *d* bonds could be due to the unusual hybridization of the C orbitals in the central four-membered ring. The rectangular shape of the central ring demands that the σ orbitals in the C_4 ring have a high *p* character consequently leading to an abnormally high *s* character in the *d* bonds; this would necessarily lead to some shortening of these bonds but would leave *b* unaffected, as found. The molecular-orbital calculations suggest a π contribution to the *e* bonds but in all three biphenylenes these bonds are longer than calculated. Although the high *p* character in *e* will lead to some increase in *e* relative to normal (*i.e.* sp^2-hybridized) C—C bond lengths, the very considerable difference between the calculated and observed values of *e* (*ca* 0·055–0·060 Å) makes one question the presence of any significant π interaction across the bridge bonds between the benzenoid rings. Other workers have suggested previously that conjugation across the C_4 ring in octafluorobiphenylene is best ignored.

As in $C_{12}H_8$ and $C_{12}F_8$, a notable feature in the structure of octamethylbiphenylene is the extremely small value [mean 115·0 (4)°] of the θ angles (Fig. 1); again this is no doubt due to the presence of the rectangular C_4 ring strongly dictating the values of the θ and φ angles. Methyl groups in adjacent positions in a benzenoid ring have their H atoms as far apart as possible when eclipsed, unlike the situation in sp^3-hybridized-C systems. Although the methyls on C(5) and C(6) are eclipsed (Fig. 1), surprisingly all the others are staggered. Steric interaction in this less favourable staggered conformation is reduced in the molecule by angles C(4)—C(3)—C(7), C(5)—C(4)—C(8) and C(4)—C(5)—C(9) all having values greater than 120°. The steric strain between the staggered methyls on C(3) and C(4) is further reduced by a comparatively long bond [1·436 (5) Å] between these two C atoms. The value of 121·4 (4)° for angle C(2)—C(3)—C(7) relative to 123·4 (4)° for angle C(1)—C(6)—C(10) [*cf.* average value of 124·7 (4)° for these angles in perfluorobiphenylene] may again reflect the larger steric strain between staggered, rather than eclipsed, methyl groups.

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Structural and Electronic Analysis of 7-Phenyltriazolo[4,3-*b*]pyridazine, a Benzodiazepine Receptor Ligand

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Abstract. $C_{11}H_8N_4$, $M_r = 196·2$, monoclinic, $P2_1/c$, $a = 20·048$ (2), $b = 7·295$ (2), $c = 13·524$ (2) Å, $\beta = 107·42$ (4)°, $V = 1887·2$ Å^3, $Z = 8$, $D_x = 1·38$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1·54178$ Å, $\mu = 6·28$ cm^{-1}, $F(000) = 816$, $T = 293$ K, final $R = 0·046$ for 3003 observed reflections [$I \geq 2·5\sigma(I)$]. The electronic structure determined by non-empirical calculations is compared with those of pyridazine and aminopyridazine. Fusion of triazole with a pyridazine ring decreases the aromaticity of the latter.

Introduction. We report here the X-ray crystal structure of a substituted triazolopyridazine. This work is part of a structure–activity-relationship study on

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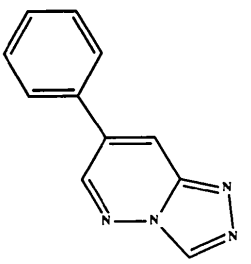
ligands of benzodiazepine receptors. Benzodiazepines are a class of psychotherapeutic drugs which present saturable high-affinity recognition sites in the central nervous system (Squires & Braestrup, 1977; Möhler & Okada, 1977). Benzodiazepines and their agonists are anxiolytic and anticonvulsant. The title compound belongs to a new family of molecules characterized by a good affinity for benzodiazepine receptor sites. However, its action profile differs from typical benzodiazepines. It appears to be antagonist (*i.e.* able to hinder benzodiazepine effects without showing any other significant biological effect).



Experimental. Crystal obtained by slow evaporation of an acetone solution at room temperature. Colourless prismatic crystal, $0{\cdot}47 \times 0{\cdot}36 \times 0{\cdot}20$ mm, for all X-ray measurements, D_m not measured. Four-circle Enraf–Nonius diffractometer (CAD-4 system, graphite monochromator). Lattice parameters from least-squares refinement of 25 medium-angle reflections. ω–2θ scan, $4 \le 2\theta \le 144°$, $[(\sin\theta)/\lambda]_{max} = 0{\cdot}62$ Å^{-1}; $-24 \le h \le 24$, $-9 \le k \le 0$, $0 \le l \le 16$. Lorentz and polarization corrections. No absorption correction. 3706 reflections measured, 3003 observed $[I \ge 2{\cdot}5\sigma(I)]$, no significant variation in intensity of one standard reflection. Direct methods: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All 30 non-H atoms found in a difference Fourier map. Full-matrix least-squares refinement on F using the *SHELX*76 program (Sheldrick, 1976). All H atoms located on a difference Fourier map. Anisotropic temperature factors (U_{ij}) for heavy atoms. Isotropic ones for H atoms (isotropic temperature factors of the carrier atoms were incremented by 0·02 Å^2). Final $R = 0{\cdot}046$ and $wR = 0{\cdot}062$; $w = 1/[\sigma^2(F) + 0{\cdot}05F^2]$, $(\Delta/\sigma)_{max} = 0{\cdot}168$ [parameter y of N(2)]. $S = 1{\cdot}31$; $-0{\cdot}23 \le \Delta\rho \le 0{\cdot}17$ e Å^{-3} in final difference map. Scattering factors from *SHELX*. Structural analysis by *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Non-empirical calculations performed with the *GAUSSIAN*82 program (Binkley, Frisch, De Frees, Raghavachari, Whiteside, Schlegel, Fluder & Pople, 1983) using the widely adopted STO-3G basis set and adapted to an IBM 4341-2 (under VM/CMS) computer.

Discussion. Atomic parameters are given in Table 1.* Atoms of the second molecule in the asymmetric unit are numbered from N(16) to C(30). Atomic numbering, bond lengths, and valence angles of both molecules in the asymmetric unit are summarized in Fig. 1. All atoms of the triazolopyridazine moiety lie in the same plane. This planarity is quantified by the deviations from the mean planes as summarized in Table 2. The phenyl ring is slightly inclined with a C(6)–C(7)–C(10)–C(11) torsion angle equal to −18·0 (2) and −28·0 (3)° for each molecule. There is no conjugation between the phenyl and the triazolopyridazine rings. The C(7)–C(10) bond lengths, 1·474 (11) and 1·480 (4) Å, are typical of a single bond between two sp^2-hybridized carbons. The corresponding standard value (Sutton, 1958) is equal to 1·466 (5) Å. Crystal packing is due solely to van der Waals interactions. This could explain the quasi-coplanarity of the molecules, assembled as 'plates'.

Although some bond lengths are determined with high estimated standard deviations, there is a good agreement between the values obtained for both molecules in the asymmetric unit.

The cyclization of an aminopyridazine into a triazolopyridazine leads to a loss of aromaticity within the pyridazine. Indeed, the N(4)–N(5) bond lengths are equal to 1·362 (4) and 1·368 (3) Å *versus* 1·347 (4) Å for 3-amino-6-phenylpyridazine (Van Der Brempt, Evrard & Durant, 1986), whereas the N(5)–C(6) bond lengths still stay very short: 1·303 (9) and 1·291 (3) Å compared with 1·308 (6) Å for the aminopyridazine. The values reported for this particular aminopyridazine are typical of a large series of various derivatives (Van Der Brempt, 1986). The C(6)–C(7) bond lengths are longer, 1·440 (6) and 1·445 (11) Å, instead of 1·415 (7) Å. The alternation between single and double bonds is thus more underlined in the title compound than in classical aminopyridazines. The same conclusions are true for the triazole ring. The single and double C–N bonds are localized.

This is also clearly demonstrated by the *ab initio* results computed within the STO-3G basis set. We present in Fig. 2 the π-electron overlap populations determined by the Mulliken (1955) charge population analysis for the pyridazine ring, 3-amino-6-phenylpyridazine (Van Der Brempt, 1986), and the title compound. These values indicate the degree of delocalization. The results obtained for the phenyl moieties, *ca* 0·21 e, are useful to give a numerical idea of good aromaticity. The π-electron overlap population values of the C–C bond in pyridazine are between 0·20

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51065 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and* B_{eq} *values with e.s.d.'s in parentheses*

$B_{eq} = 8\pi^2 U_{eq}(\text{Å}^2)$; $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B_{eq}
N(1)	8913 (1)	4088 (1)	4472 (1)	6·21 (1)
N(2)	8199 (1)	3860 (1)	4101 (1)	6·69 (1)
C(3)	7961 (1)	3531 (2)	4883 (1)	6·12 (1)
N(4)	8503 (1)	3518 (1)	5773 (1)	4·75 (1)
N(5)	8485 (1)	3185 (1)	6754 (1)	5·87 (1)
C(6)	9097 (1)	3223 (1)	7447 (1)	5·36 (1)
C(7)	9754 (1)	3598 (1)	7260 (1)	4·29 (1)
C(8)	9740 (1)	3944 (1)	6262 (1)	4·72 (1)
C(9)	9089 (1)	3877 (1)	5480 (1)	4·68 (1)
C(10)	409 (1)	3586 (1)	8126 (1)	4·71 (1)
C(11)	406 (1)	3725 (2)	9150 (1)	6·78 (1)
C(12)	11022 (1)	3697 (2)	9958 (1)	8·35 (1)
C(13)	11656 (1)	3539 (2)	9764 (1)	8·34 (1)
C(14)	11673 (1)	3420 (2)	8751 (1)	8·26 (1)
C(15)	11055 (1)	3446 (2)	7944 (1)	6·62 (1)
N(16)	5975 (1)	1295 (1)	5475 (1)	5·80 (1)
N(17)	6697 (1)	1194 (1)	5795 (1)	6·25 (1)
C(18)	6916 (1)	1003 (2)	6797 (1)	5·85 (1)
N(19)	6356 (1)	961 (1)	7171 (1)	4·90 (1)
N(20)	6355 (1)	792 (1)	8177 (1)	5·63 (1)
C(21)	5738 (1)	838 (1)	8291 (1)	5·20 (1)
C(22)	5084 (1)	1028 (1)	7476 (1)	4·40 (1)
C(23)	5117 (1)	1182 (1)	6489 (1)	4·76 (1)
C(24)	5778 (1)	1158 (1)	6320 (1)	4·60 (1)
C(25)	4417 (1)	968 (1)	7734 (1)	4·63 (1)
C(26)	4377 (1)	1514 (1)	8701 (1)	5·47 (1)
C(27)	3759 (1)	1388 (2)	8945 (1)	6·60 (1)
C(28)	3166 (1)	722 (2)	8224 (1)	7·14 (1)
C(29)	3194 (1)	196 (2)	7253 (1)	6·84 (1)
C(30)	3809 (1)	329 (1)	7001 (1)	5·54 (1)

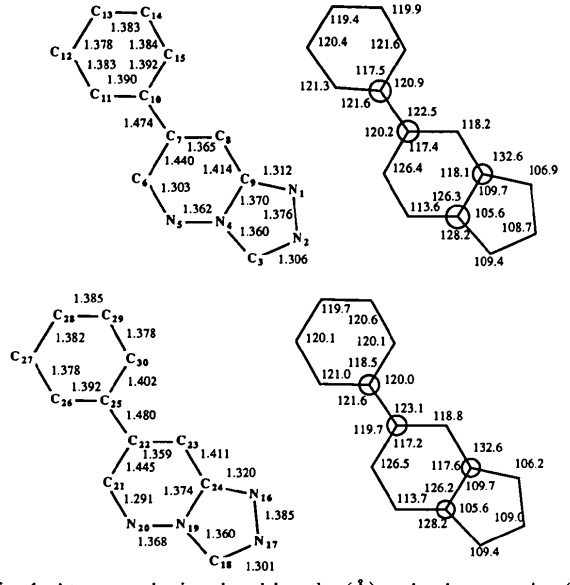


Fig. 1. Atom numbering, bond lengths (Å) and valence angles (°) for both molecules in the asymmetric unit. Maximum e.s.d.'s are 0·011 Å and 0·2°.

Table 2. *Deviations* (Å) *from mean planes defined by* (*a*) *the pyridazine atoms and* (*b*) *the triazole atoms* (*results for both molecules in the asymmetric unit*)

(*a*)	N(1)	−0·041	N(16)	0·015
	N(2)	−0·054	N(17)	0·027
	C(3)	−0·022	C(18)	0·022
	N(4)	0·001	N(19)	−0·001
	N(5)	0·006	N(20)	−0·003
	C(6)	−0·006	C(21)	0·003
	C(7)	−0·002	C(22)	0·001
	C(8)	0·009	C(23)	−0·003
	C(9)	−0·008	C(24)	0·003
(*b*)	N(1)	0·001	N(16)	−0·001
	N(2)	−0·002	N(17)	−0·001
	C(3)	0·003	C(18)	0·002
	N(4)	−0·002	N(19)	−0·003
	N(5)	−0·030	N(20)	0·007
	C(6)	−0·063	C(21)	0·029
	C(7)	−0·050	C(22)	0·030
	C(8)	−0·005	C(23)	0·013
	C(9)	0·001	C(24)	0·003

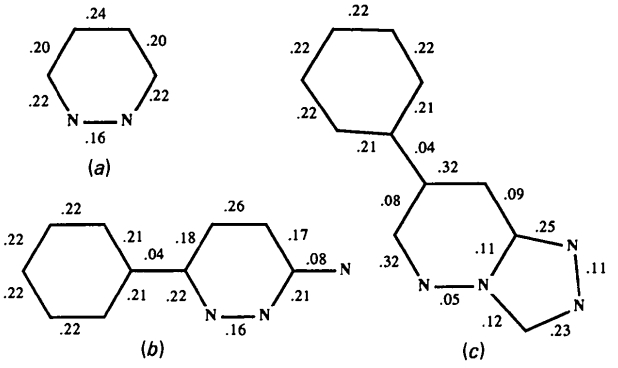


Fig. 2. π-electron overlap populations (e) of (*a*) pyridazine, (*b*) 3-amino-6-phenylpyridazine, and (*c*) the title compound.

and 0·24 e, whereas the N–N value is equal to 0·16 e. The conjugation of an amine function with the pyridazine ring leads to a weak perturbation, at most 0·03 e, of the pyridazinic aromaticity. However, in the case of the triazolopyridazine, the alternation of double (*ca* 0·32 e) and single (*ca* 0·10 e) bonds is clear. Similar results have been obtained for 3-methyl-6-phenyl and 3-methyl-7-phenyl analogs (results to be published); the study of these compounds shows that the position of the phenyl ring has no effect on the delocalization within the triazolopyridazine moiety.

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The Structure of L-α-Aminoadipic Acid

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Abstract. $C_6H_{11}NO_4$, $M_r = 161{\cdot}16$, monoclinic, $P2_1$, $a = 5{\cdot}136\ (3)$, $b = 6{\cdot}992\ (2)$, $c = 10{\cdot}065\ (10)$ Å, $\beta = 93{\cdot}32\ (5)°$, $U = 360{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}48$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 172$, $T = 293$ K. $R = 0{\cdot}058$ for 305 unique observed $[F > 5\sigma(F)]$ reflections. L-α-Aminoadipic acid exists as a zwitterion. The conformation around the amino terminus is similar to that of L-glutamic acid. There is a short intermolecular hydrogen bond between the carboxyl groups.

Introduction. Amino acids are precursors for proteins, hormones and neurotransmitters and can be neurotransmitters themselves. Membrane systems that make up different tissues in the body appear to be selective in the amino acids that they are able to recognize and take up. One example is the brain, where glutamate is an important excitatory amino acid and which has specific receptors for glutamate (Watkins & Olverton, 1987). Another example is the range of amino-acid transport mechanisms that exist for the import and export of amino acids in tissues such as liver, muscle *etc.* Such transport of amino acids is important for the amino-acid economy of the body and the description of the interaction between amino acids or analogues and receptors may prove important for altering the uptake or efflux of an amino acid from a particular organ (Rennie *et al.*, 1986). A knowledge of the molecular structure of naturally occurring amino acids or their analogues is necessary in order to understand and predict the necessary characteristics of an amino-acid agonist or antagonist, *i.e.* to be able to say whether a chemical substance will interact solely because of its shape or whether there are required chemical groups in the molecule before binding can take place. This may in turn give some insight into the nature of the receptive site for the molecule. We investigate here the structure of the amino acid L-2α-aminoadipic acid, an analogue of glutamic acid.

Experimental. Crystals were obtained from aqueous solution. Space group and initial cell dimensions were obtained from Weissenberg photographs. Data were collected on a Nicolet *P*3 (four-circle) diffractometer in Aberdeen by RAH. The crystal had dimensions $0{\cdot}175 \times 0{\cdot}1 \times 0{\cdot}04$ mm. Cell parameters were measured on the diffractometer using 14 reflections in the 2θ range 12–14°. Range of indices: $0 \le h \le 7$; $0 \le k \le 9$; $-13 \le l \le 13$. Data measured using $\omega/2\theta$ scans in the range $0 < 2\theta < 50°$. Standard reflections 020 and 120 were measured every 50 reflections. No changes greater than 2σ from the mean of the intensities of these

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