Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.7117 (7)	1.0866 (4)	0.4420 (2)	0.0676 (12)
O2	1.0278 (6)	0.9766 (3)	0.4734 (2)	0.0552 (10)
O3	0.8244 (7)	0.7776 (4)	0.26805 (15)	0.0691 (12)
O4	0.5320 (10)	0.6655 (8)	0.2186 (2)	0.129 (2)
N1	1.0423 (9)	0.6325 (5)	0.4296 (2)	0.0671 (14)
C1	0.7681 (8)	0.8440 (5)	0.4168 (2)	0.0424 (11)
C2	0.6269 (9)	0.8505 (6)	0.3586 (2)	0.0500 (13)
C3	0.5161 (9)	0.8096 (6)	0.4163 (2)	0.0592 (14)
C4	0.8305 (9)	0.9824 (5)	0.4453 (2)	0.0466 (12)
C5	1.1037 (12)	1.1053 (6)	0.5037 (3)	0.079 (2)
C6	0.9234 (9)	0.7275 (6)	0.4245 (2)	0.0485 (12)
C7	0.6540 (9)	0.7401 (5)	0.3102 (2)	0.0520 (14)
C8	0.4418 (12)	0.7214 (9)	0.2722 (3)	0.091 (2)
C9	0.7581 (16)	0.7300 (8)	0.2093 (3)	0.086 (2)
C10	0.8931 (14)	0.6037 (8)	0.1906 (4)	0.099 (3)
C11	0.7640 (4)	0.8389 (10)	0.1674 (4)	0.317 (15)

Table 4. *Geometric parameters (Å, °) for (II)*

O1—C4	1.211 (6)	C1—C4	1.496 (7)
O2—C4	1.322 (6)	C1—C3	1.525 (7)
O2—C5	1.457 (6)	C1—C2	1.534 (7)
O3—C7	1.416 (6)	C2—C3	1.483 (7)
O3—C9	1.426 (7)	C2—C7	1.500 (7)
O4—C8	1.401 (7)	C7—C8	1.518 (8)
O4—C9	1.483 (10)	C9—C11	1.382 (11)
N1—C6	1.146 (6)	C9—C10	1.494 (10)
C1—C6	1.443 (7)		
C4—O2—C5	116.9 (4)	O1—C4—C1	122.8 (5)
C7—O3—C9	108.8 (5)	O2—C4—C1	112.2 (4)
C8—O4—C9	107.8 (5)	N1—C6—C1	177.9 (5)
C6—C1—C4	117.4 (4)	O3—C7—C2	111.6 (4)
C6—C1—C3	117.4 (4)	O3—C7—C8	104.8 (4)
C4—C1—C3	115.5 (4)	C2—C7—C8	112.6 (5)
C6—C1—C2	118.4 (4)	O4—C8—C7	101.3 (5)
C4—C1—C2	116.8 (4)	C11—C9—O3	111.4 (7)
C3—C1—C2	58.0 (3)	C11—C9—O4	114.9 (11)
C3—C2—C7	118.5 (5)	O3—C9—O4	104.6 (5)
C3—C2—C1	60.7 (3)	C11—C9—C10	113.4 (9)
C7—C2—C1	120.6 (4)	O3—C9—C10	110.8 (6)
C2—C3—C1	61.3 (3)	O4—C9—C10	101.0 (6)
O1—C4—O2	125.0 (5)		
C6—C1—C2—C7	−1.4 (7)	C3—C2—C7—O3	−159.9 (4)
C5—O2—C4—C1	−179.0 (4)	C1—C2—C7—C8	153.5 (5)

For both compounds, data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989); software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1282). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Strained Tricyclic Product of a Dipolar 1,3-Cycloaddition Reaction of Diazepine

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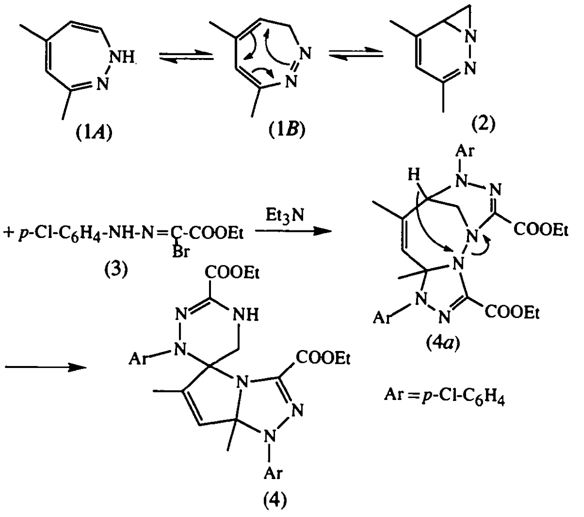
Abstract

In the title compound, diethyl 1,1′-bis(*p*-chlorophenyl)-6,7a-dimethyl-4,7a,1′,4′,5′,6′-hexahydropyrrolo[4,5-*a*]-[1,2,4]triazole-5-spiro-6′-[1,2,4]triazine-3,3′-dicarboxylate, $C_{27}H_{28}Cl_2N_6O_4$, the tricyclic system is composed of two five-membered rings sharing one side and one six-membered ring having one C atom in common with one of the five-membered rings. Strain in this molecule is reflected by significant variations in the bond distances and bond angles.

Comment

We report here the dipolar 1,3-cycloaddition reaction of diazepine, (1), [which can exist in the tautomeric forms (1*A*) and (1*B*)] with the *N*-aryl-*C*-ethoxycarbonyl nitrilimine, (3), according to the reaction scheme below. The resulting cycloaddition product, (4), corresponds to a double cycloaddition onto a diazanorcaradiene form, (2), and it involves a rearrangement of the initial adduct, (4*a*), to give the tricyclic system with a spiro-type structure. The existence of this structure which was postulated by Anderson, Sharp & Strathdee (1979) is confirmed here.



Two chlorophenyl, two ethylcarboxy ether and two methyl groups are attched to the three-ring system which is composed of two five-membered rings sharing one side (N4—C5) and one six-membered ring with one C atom (C8) in common with one of the five-membered rings. Each of these three rings contains one double bond so a high degree of planarity is expected, as indicated by torsion angles and distances to least-squares planes. Thus, the N_3C_2 ring has an envelope conformation with C5 lying 0.398 (4) Å out of the mean plane of the other four atoms (r.m.s. Δ = 0.016 Å). The six-membered N_3C_3 ring has five atoms in a plane (r.m.s. Δ = 0.012 Å) with C13 displaced 0.598 (4) Å from it. The second five-membered ring is more distorted, as indicated by the torsion angles N4—C5—C6—C7 and C5—C6—C7—C8 of 7.5 (4) and 9.2 (4)°, respectively. This ring can therefore be described either as a distorted envelope [the N4 atom being 0.371 (3) Å out of the mean plane of the four C atoms (r.m.s. Δ = 0.077 Å)] or as a twisted half-chair with N4 on one side [−0.187 (3) Å] and C8 on the other side [0.231 (4) Å] of the plane containing C5, C6 and C7. Significant variations in bond distances and bond angles reflect the strain in the molecule. Thus, the Nsp^3—Csp^3 bonds (N4—C5 and N4—C8) are somewhat different [1.474 (4) and 1.500 (5) Å, respectively] and two of the Nsp^2—Csp^2 bonds (N1—C14 and N9—C20) are 1.394 (5) and 1.418 (5) Å, respectively, but the third (C11—N12) is only 1.359 (5) Å. The three Csp^3—Csp^2 bonds range from 1.491 (5) to 1.525 (6) Å [mean value 1.51 (2) Å] and the three Nsp^2—Csp^3 bonds range from 1.445 (6) to 1.510 (5) Å [mean value 1.47 (4) Å]. The sp^2 atom N2 has a ring bond angle of 106.4 (3)° and the sp^3 atom C5 has a ring bond angle of 99.7 (3)°, almost 10° below the normal tetrahedral value. The aryl and ester substituents are all approximately coplanar with their respective rings.

Hydrogen bonding links molecules into pairs with two hydrogen bonds related by a centre of symmetry: an intermolecular distance of 2.942 (4) Å is observed between O3 and N12^i [symmetry code: (i) $2 - x$, $-y$, $1 - z$), with O3···H12^i = 2.11 Å and O3···H12^i—N12^i = 157° for this hydrogen bond.

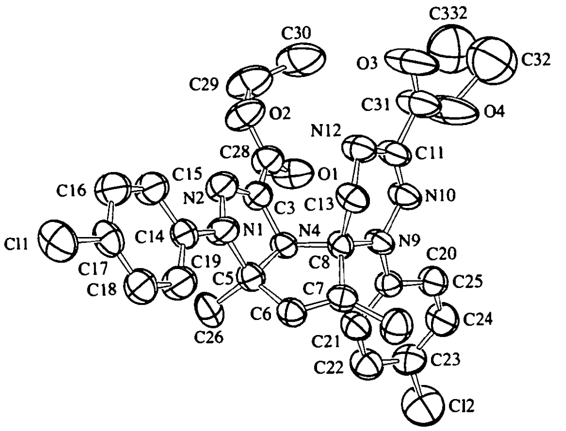


Fig. 1. View of the molecular structure, ellipsoids drawn at the 50% probability level, showing the atomic numbering scheme.

Experimental

To a solution of 0.7 g (5.7 mmol) diazepine and 3.6 g (11.72 mmol) arylhydrazono-α-bromoglyoxylate ether in 40 ml dry benzene were added 3 ml of triethylamine dissolved in 10 ml of dry benzene. The mixture was stirred for 3 d, washed three times with 100 ml water, and dried over sodium sulfate. The organic phases were concentrated and the crude product was chromatographed on silica gel (Merck 60), with diethyl ether/petroleum ether, first 3:7, then 6:4. The final product (4) was obtained in 65% yield (m.p. 451–452 K). All analytical and spectral data (MS, ^{1}H and ^{13}C NMR) are in agreement with the structure. (4) was dissolved at 308 K in diethyl ether/ethanol (95:5). Crystals were obtained by slowly decreasing the temperature to 293 K.

Crystal data

$C_{27}H_{28}Cl_2N_6O_4$
M_r = 571.47
Monoclinic
$P2_1/n$
a = 9.841 (1) Å
b = 21.845 (2) Å
c = 13.015 (3) Å
β = 94.43 (5)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–15°
μ = 0.274 mm^{-1}
T = 294 K
Prismatic

$V = 2789\ (2)$ Å^3
$Z = 4$
$D_x = 1.361$ Mg m^{-3}
D_m not measured

0.40 × 0.35 × 0.30 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4707 measured reflections
4351 independent reflections
2742 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.025$
$\theta_{\text{max}} = 24°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 14$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.057$
$wR = 0.082$
$S = 2.885$
2742 reflections
351 parameters
H atoms: see text
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\text{max}} = 0.084$
$\Delta\rho_{\text{max}} = 0.56$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.31$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.1166 (1)	0.08994 (5)	0.13430 (9)	0.0772 (3)
Cl2	1.2353 (2)	0.47309 (6)	0.5388 (1)	0.1129 (5)
O1	0.9027 (3)	0.1829 (1)	0.6659 (2)	0.0749 (9)
O2	0.7669 (3)	0.1004 (1)	0.6644 (2)	0.0785 (9)
O3	1.1539 (4)	0.0222 (1)	0.5605 (3)	0.123 (1)
O4	1.2888 (4)	0.0994 (2)	0.6130 (3)	0.148 (1)
N1	0.6032 (3)	0.1700 (2)	0.3914 (2)	0.0589 (9)
N2	0.6366 (3)	0.1413 (2)	0.4836 (2)	0.061 (1)
N4	0.7949 (3)	0.2164 (1)	0.4642 (2)	0.0446 (8)
N9	1.0442 (3)	0.2197 (1)	0.4570 (2)	0.0503 (9)
C3	0.7464 (4)	0.1673 (2)	0.5228 (3)	0.052 (1)
C5	0.6779 (4)	0.2304 (2)	0.3903 (3)	0.049 (1)
C6	0.7438 (3)	0.2478 (2)	0.2951 (3)	0.047 (1)
C7	0.8763 (4)	0.2382 (2)	0.3040 (3)	0.047 (1)
C8	0.9141 (3)	0.2026 (2)	0.4028 (3)	0.045 (1)
N10	1.1300 (3)	0.1775 (1)	0.5077 (3)	0.060 (1)
C11	1.0940 (4)	0.1212 (2)	0.5065 (3)	0.061 (1)
N12	0.9774 (3)	0.0988 (1)	0.4578 (3)	0.062 (1)
C13	0.9231 (4)	0.1352 (2)	0.3715 (3)	0.056 (1)
C14	0.4841 (4)	0.1529 (2)	0.3335 (3)	0.050 (1)
C15	0.4120 (4)	0.1024 (2)	0.3615 (3)	0.065 (1)
C16	0.2978 (4)	0.0830 (2)	0.3011 (4)	0.071 (1)
C17	0.2576 (4)	0.1151 (2)	0.2126 (3)	0.057 (1)
C18	0.3260 (4)	0.1661 (2)	0.1852 (3)	0.063 (1)
C19	0.4401 (4)	0.1849 (2)	0.2460 (3)	0.069 (1)
C20	1.0855 (4)	0.2811 (2)	0.4762 (3)	0.046 (1)
C21	0.9963 (4)	0.3297 (2)	0.4654 (3)	0.056 (1)
C22	1.0418 (4)	0.3892 (2)	0.4862 (3)	0.063 (1)
C23	1.1758 (4)	0.3989 (2)	0.5168 (3)	0.063 (1)
C24	1.2654 (4)	0.3510 (2)	0.5273 (4)	0.072 (1)
C25	1.2213 (4)	0.2925 (2)	0.5070 (3)	0.060 (1)
C26	0.5883 (4)	0.2807 (2)	0.4302 (3)	0.064 (1)
C28	0.8150 (4)	0.1517 (2)	0.6250 (3)	0.059 (1)
C30	0.9622 (7)	0.0625 (3)	0.7752 (5)	0.127 (2)
C31	1.1820 (5)	0.0757 (2)	0.5636 (4)	0.093 (2)
C29	0.8209 (6)	0.0863 (2)	0.7701 (4)	0.100 (2)
C27	0.9789 (4)	0.2541 (2)	0.2289 (3)	0.064 (1)
C32	1.4161 (8)	0.0489 (4)	0.6479 (7)	0.159 (3)
C332	1.358 (1)	0.0529 (5)	0.7387 (9)	0.160 (4)
C331	1.451 (3)	0.051 (1)	0.738 (2)	0.143 (9)

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

N1—N2	1.372 (4)	C3—C28	1.484 (5)
N1—C5	1.510 (5)	C5—C6	1.491 (5)
N1—C14	1.394 (5)	C6—C7	1.316 (5)
N2—C3	1.290 (5)	C7—C8	1.525 (5)
N4—C3	1.420 (5)	C7—C27	1.499 (6)
N4—C5	1.474 (4)	C8—C13	1.532 (5)
N4—C8	1.500 (5)	N10—C11	1.280 (5)
N9—C8	1.462 (4)	C11—N12	1.359 (5)
N9—N10	1.382 (4)	C11—C31	1.480 (6)
N9—C20	1.418 (5)	N12—C13	1.445 (5)
N2—N1—C5	108.9 (3)	C5—C6—C7	112.2 (3)
N1—N2—C3	106.4 (3)	C6—C7—C8	109.3 (3)
C3—N4—C5	103.3 (3)	N4—C8—C7	101.4 (3)
C5—N4—C8	107.3 (3)	N9—C8—C13	107.9 (3)
C8—N9—N10	122.7 (3)	N9—N10—C11	118.5 (3)
N2—C3—N4	115.2 (3)	N10—C11—N12	125.1 (4)
N1—C5—N4	99.7 (3)	C11—N12—C13	114.4 (3)
N4—C5—C6	103.2 (3)	C8—C13—N12	110.4 (3)
N1—N2—C3—N4	2.0 (4)	N4—C5—C6—C7	7.5 (4)
C8—N9—N10—C11	0.4 (5)	C5—C6—C7—C8	9.2 (4)
N9—N10—C11—N12	0.8 (6)		

The H atom attached to N12 was located by difference synthesis in the C11—N12—C13 plane, making angles of ~120° with C11—N12 and N12—C13 and thus confirming the sp^2 character of N12. The other H atoms were introduced at idealized positions but not refined. The ethyl group attached to O4 is disordered, contributing to the relatively high value of R. It was possible to resolve the terminal methyl into two sites, C331 and C332, each of occupancy 0.5, but the geometry involving C32 and C33 was not realistic. The H atoms of this group were omitted.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP BEGIN* (Frenz *et al.*, 1985). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SDP LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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