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4-[5′-Oxo-1′,3′-diphenyl-4′-(*p*-tolylmethyl)]-1,3-diphenyl-4-(*p*-tolylmethyl)pyrazol-5-one: Product of a Reductive Dimerization Reaction

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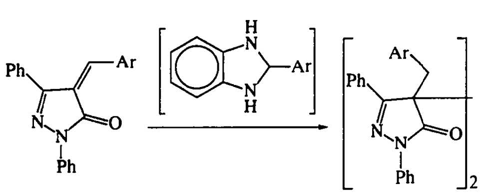
Abstract

The title compound, 2,5,2′,5′-tetraphenyl-4,4′-bis(*p*-tolylmethyl)-[4,4′-bipyrazolyl]-3,3′(2*H*,2′*H*)-dione, $C_{46}H_{38}N_4O_2$, isolated in the *dl* form by a diastereoselective reductive dimerization of 4-arylmethylene-3-phenylpyrazol-5-one, is a dimeric compound with approximate C_2 symmetry. It contains two chiral C atoms having the same configuration and related by the pseudo-twofold axis. The crystal consists of a centrosymmetric crystal packing of both *R,R* and *S,S* diastereomers.

Comment

During our studies on the reactivity of 4-arylmethylene-azol-5-ones, we had to consider the reductive dimerization of 4-arylmethylene-1,3-diphenylpyrazol-5-ones, (1), and the stereochemistry of the C,C-linked dimers, (2), obtained according to the scheme below, with 2-arylbenzimidazoline being generated *in situ via* a single-electron transfer process (Risitano, Grassi, Caruso & Foti, 1996).



(1) (2)

Unlike the oxidation reactions of the 4-arylmethyl-pyrazol-5-ones, which lead to *meso* and *dl* mixtures of analogous dimers (Veibel, 1972), we have always observed a highly stereoselective pathway with isolation of one diastereomeric form. Therefore, considering previous dubious stereochemical assignations, we undertook the X-ray crystal structure analysis of the title dimer [(2); Ar = C_6H_4-*p*-Me], for which suitable single crystals were obtained.

The molecular conformation of the title compound is shown in Fig. 1. The molecule possesses an approximate twofold symmetry, with the pseudo-binary axis passing through the midpoint of the central C5—C35 bond [1.571 (9) Å]. Since the central C atoms are related by this pseudo-C_2 axis, they must possess the same chirality and the molecule must therefore have either *R,R* or *S,S* chirality. Owing to the space-group centrosymmetry, both the *R,R* and *S,S* enantiomers are present in the crystal (the *S,S* configuration is represented in Fig. 1).

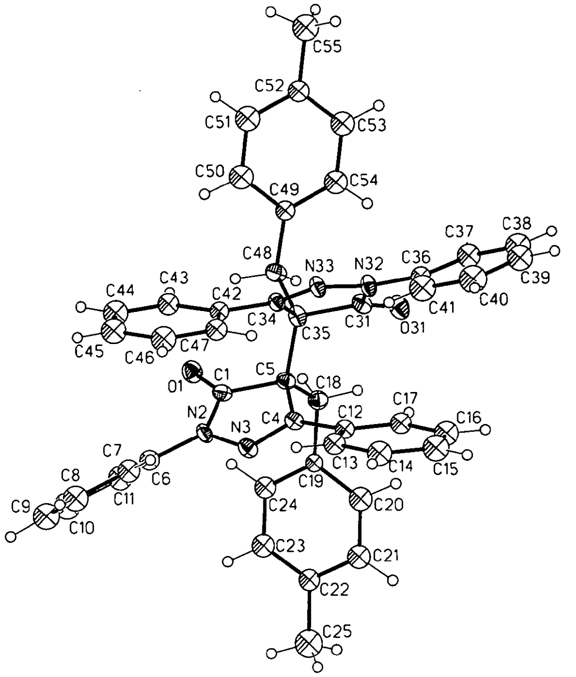


Fig. 1. Perspective view of the title dimer showing the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, while H-atom size is arbitrary.

As expected, the pyrazolone rings are flat [the maximum deviation from each mean plane is 0.021 (6) Å] and form a dihedral angle of 54.5 (2)° with one another. The central core of the molecule is composed of two 4-arylmethylene-1,3-diphenylpyrazol-5-one fragments whose geometries are almost equal, as can be seen by a comparison of the corresponding bond distances and angles. The two pyrazolone rings are slightly rotated with respect to the C5—C35 bond from C_2 symmetry [C31—C35—C5—C1 −175.9 (5)°] and the distortion might be related to the steric hindrance of the monomers, implied by the short C4···C34 contact of 2.846 (9) Å. Such an arrangement is also advantageous for the formation of intramolecular hydrogen bonds [H48*A*···O1 2.40, H13···N3 2.49, H18*A*···O31 2.33, H37···O31 2.46, H47···N33 2.53 and H41···N33 2.45 Å].

The two C═O bond distances are comparable and their mean value of 1.225 (8) Å is in good agreement with the corresponding value reported for a comparable pyrazolone compound (Aly *et al.*, 1994). The sums of the valence angles around both the N2 and N32 atoms (360.0 and 359.2°, respectively) confirm the nitrogen sp^2 hybridization, as expected by the amidic delocalization. The N32 amide fragment appears to be a little more deformed from planarity than the N2 amide fragment, as evidenced by the corresponding O═C—N—C_{phen} torsion angles of 10 (1) and 0.5 (10)°, respectively. Neither fragment is conjugated with its two attached phenyl substituents which are significantly rotated with respect to their corresponding pyrazolone ring. This interruption of the delocalization in both fragments is confirmed both by the length of the bonds to the phenyl groups and by the angles between the phenyl and pyrazolone mean planes; the amidic N atoms show N2—C6 = 1.423 (8) *versus* N32—C36 = 1.427 (8) Å, with corresponding dihedral angles of 39.9 (2) *versus* 28.0 (2)°, while for the C-bonded phenyl substituents, the distances are C4—C12 = 1.482 (8) *versus* C34—C42 = 1.466 (9) Å, with dihedral angles of 29.2 (2) *versus* 33.6 (2)°. Steric hindrance may be responsible for the significant asymmetry of the pyrazolone exocyclic bond angles at the *N*-phenyl substituents; at the amidic N2 and N32 atoms the angle difference is 12.5 (5) *versus* 9.4 (5)°. The remaining bond lengths and angles have expected values.

The molecular packing is essentially due to van der Waals interactions as well as to weak inter- and intramolecular hydrogen bonds (these are reported in the supplementary material).

Experimental

The title compound was prepared according to a previously published method (Risitano, Grassi, Caruso & Foti, 1996)

Crystal data

$C_{46}H_{38}N_4O_2$
$M_r = 678.832$
Monoclinic
$P2_1/n$
$a = 9.420\,(1)$ Å
$b = 20.130\,(3)$ Å
$c = 18.887\,(3)$ Å
$\beta = 95.10\,(1)°$
$V = 3567.3\,(9)$ Å^3
$Z = 4$
$D_x = 1.264$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 7.5–15.0°$
$\mu = 0.0781$ mm^{-1}
$T = 298$ K
Almost cubic
0.24 × 0.22 × 0.21 mm
White

Data collection

Siemens *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8293 measured reflections
6309 independent reflections
2107 observed reflections [$F > 7\sigma(F)$]

$R_{int} = 0.0115$
$\theta_{max} = 25°$
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 21$
3 standard reflections monitored every 97 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0618$
$wR = 0.0716$
$S = 1.84$
2107 reflections
290 parameters
H atoms riding, with fixed isotropic U
$w = 1/[\sigma^2(F) + 0.00052F^2]$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 0.00059 (15)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for O1 to C55, U_{iso} for all others.

	x	y	z	U_{eq}/U_{iso}
O1	−0.1814 (5)	0.7488 (2)	0.0342 (2)	0.042 (2)
C1	−0.0920 (7)	0.7534 (3)	0.0859 (3)	0.033 (2)
N2	−0.0561 (6)	0.7045 (2)	0.1335 (3)	0.033 (2)
N3	0.0476 (6)	0.7245 (3)	0.1867 (3)	0.036 (2)
C4	0.0864 (7)	0.7845 (3)	0.1736 (3)	0.030 (2)
C5	0.0041 (7)	0.8130 (3)	0.1067 (3)	0.031 (2)
C18	0.0953 (8)	0.8237 (3)	0.0422 (3)	0.041 (3)
C25	0.486 (1)	0.6115 (4)	−0.0251 (4)	0.078 (4)
O31	0.0888 (5)	0.9648 (2)	0.0983 (2)	0.043 (2)
C31	0.0146 (7)	0.9376 (3)	0.1391 (3)	0.032 (2)
N32	−0.0033 (6)	0.9569 (3)	0.2071 (3)	0.035 (2)
N33	−0.0953 (6)	0.9154 (3)	0.2406 (3)	0.035 (2)
C34	−0.1450 (7)	0.8708 (3)	0.1958 (3)	0.030 (2)
C35	−0.0832 (7)	0.8767 (3)	0.1235 (3)	0.031 (2)
C48	−0.1951 (7)	0.8976 (3)	0.0614 (3)	0.040 (3)
C55	−0.5528 (9)	1.1290 (4)	0.1064 (4)	0.072 (3)
C37	0.1281 (8)	1.0611 (3)	0.2187 (4)	0.050 (2)
C12	0.1931 (7)	0.8165 (3)	0.2251 (3)	0.032 (2)
C13	0.1981 (8)	0.7944 (3)	0.2957 (3)	0.043 (2)
C11	−0.1338 (8)	0.6016 (4)	0.0760 (4)	0.055 (2)
C14	0.2977 (8)	0.8212 (4)	0.3461 (4)	0.056 (2)
C38	0.2041 (8)	1.1072 (4)	0.2616 (4)	0.060 (2)
C15	0.3907 (9)	0.8700 (4)	0.3273 (4)	0.064 (2)
C47	−0.2074 (8)	0.7987 (3)	0.2936 (3)	0.043 (2)
C16	0.3857 (8)	0.8921 (4)	0.2593 (4)	0.054 (2)
C39	0.2269 (8)	1.0979 (4)	0.3329 (4)	0.060 (2)
C17	0.2853 (7)	0.8660 (3)	0.2074 (3)	0.042 (2)
C51	−0.5062 (9)	1.0054 (4)	0.1059 (4)	0.058 (2)
C6	−0.1092 (7)	0.6385 (3)	0.1371 (3)	0.037 (2)
C40	0.1755 (9)	1.0425 (4)	0.3624 (5)	0.071 (3)
C54	−0.2363 (8)	1.0219 (3)	0.0675 (3)	0.051 (2)
C19	0.1946 (7)	0.7671 (3)	0.0276 (3)	0.030 (2)
C20	0.3395 (8)	0.7731 (4)	0.0411 (3)	0.052 (2)
C41	0.0974 (9)	0.9955 (4)	0.3208 (4)	0.065 (2)
C21	0.4336 (8)	0.7232 (4)	0.0241 (3)	0.052 (2)
C52	−0.4584 (8)	1.0690 (3)	0.0975 (3)	0.043 (2)
C22	0.3818 (8)	0.6649 (3)	−0.0064 (3)	0.043 (2)
C23	0.2399 (8)	0.6578 (4)	−0.0203 (3)	0.047 (2)
C42	−0.2331 (7)	0.8177 (3)	0.2221 (3)	0.033 (2)
C24	0.1456 (8)	0.7081 (3)	−0.0046 (3)	0.042 (2)
C43	−0.3386 (8)	0.7846 (3)	0.1796 (3)	0.044 (2)
C7	−0.1304 (8)	0.6117 (3)	0.2020 (4)	0.048 (2)
C53	−0.3228 (8)	1.0766 (4)	0.0787 (4)	0.054 (2)
C44	−0.4199 (8)	0.7350 (4)	0.2078 (4)	0.058 (2)
C49	−0.2836 (7)	0.9573 (3)	0.0766 (3)	0.035 (2)

C45	−0.3945 (9)	0.7170 (4)	0.2783 (4)	0.062 (2)
C8	−0.1811 (8)	0.5465 (4)	0.2059 (4)	0.060 (2)
C50	−0.4203 (8)	0.9508 (4)	0.0957 (3)	0.056 (2)
C9	−0.2048 (8)	0.5097 (4)	0.1458 (4)	0.065 (2)
C46	−0.2888 (8)	0.7484 (4)	0.3202 (4)	0.060 (2)
C10	−0.1850 (9)	0.5362 (4)	0.0810 (4)	0.067 (2)
C36	0.0752 (7)	1.0058 (3)	0.2488 (3)	0.035 (2)

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

O1—C1	1.234 (8)	C25—C22	1.52 (1)
C1—N2	1.356 (8)	O31—C31	1.215 (8)
C1—C5	1.533 (9)	C31—N32	1.367 (8)
N2—N3	1.397 (7)	C31—C35	1.547 (9)
N2—C6	1.423 (8)	N32—N33	1.395 (8)
N3—C4	1.293 (8)	N32—C36	1.427 (8)
C4—C5	1.534 (8)	N33—C34	1.294 (8)
C4—C12	1.482 (8)	C34—C35	1.535 (9)
C5—C18	1.566 (9)	C34—C42	1.466 (9)
C5—C35	1.571 (9)	C35—C48	1.563 (8)
C18—C19	1.514 (9)	C48—C49	1.505 (9)
O1—C1—C5	127.4 (6)	O31—C31—C35	127.1 (6)
O1—C1—N2	125.7 (6)	O31—C31—N32	126.5 (6)
N2—C1—C5	106.9 (5)	N32—C31—C35	106.4 (5)
C1—N2—C6	129.9 (5)	C31—N32—C36	127.8 (5)
C1—N2—N3	112.7 (5)	C31—N32—N33	113.0 (5)
N3—N2—C6	117.4 (5)	N33—N32—C36	118.4 (5)
N2—N3—C4	108.8 (5)	N32—N33—C34	108.7 (5)
N3—C4—C12	117.8 (6)	N33—C34—C42	117.8 (6)
N3—C4—C5	112.1 (5)	N33—C34—C35	112.6 (5)
C5—C4—C12	130.0 (5)	C35—C34—C42	129.0 (5)
C1—C5—C4	99.4 (5)	C31—C35—C34	99.1 (5)
C4—C5—C35	111.9 (5)	C5—C35—C34	111.3 (5)
C4—C5—C18	114.9 (5)	C5—C35—C31	111.8 (5)
C1—C5—C35	112.5 (5)	C34—C35—C48	113.8 (5)
C1—C5—C18	105.1 (5)	C31—C35—C48	106.2 (5)
C18—C5—C35	112.3 (5)	C5—C35—C48	113.5 (5)
C5—C18—C19	115.4 (5)	C35—C48—C49	114.8 (5)
O1—C1—N2—C6	−0.5 (10)	O31—C31—N32—C36	−10 (1)
N3—N2—C6—C7	38.2 (8)	N33—N32—C36—C41	22.9 (9)
N3—C4—C12—C13	−27.2 (9)	N33—C34—C42—C47	−29.3 (9)
C35—C5—C18—C19	173.7 (5)	C5—C35—C48—C49	178.3 (5)

Reflection intensities were evaluated by profile fitting of a 96-step peak scan among 2θ shells procedure (Diamond, 1969). The model of the structure, completed by a combination of least-squares techniques and difference Fourier synthesis, was refined by full-matrix least-squares methods. Owing to the small observations/parameters ratio, only the non-H atoms of the pyrazolone fragments and the C atoms of the methylene and *p*-methyl groups were refined anisotropically.

Data collection: *P3/V* (Siemens, 1989). Cell refinement: *P3/V*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus* and *PARST95* (Nardelli, 1995).

Lists of structure factors, hydrogen-bond data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1248). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.

Aly, M. F., El-Nagger, G. M., El-Emary, T. I., Grigg, R., Metwally, S. A. M. & Sivagnanam, S. (1994). *Tetrahedron*, pp. 895–906.

Diamond, R. (1969). *Acta Cryst.* A**25**, 43–55.

Nardelli, M. (1995). *PARST95* (locally modified). *J. Appl. Cryst.* **28**, 659.

Risitano, F., Grassi, G., Caruso, F. & Foti, F. (1996). *Tetrahedron*, pp. 1443–1450.

Sheldrick, G. M. (1992). *SHELXTL-Plus*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1989). *P3/V*. Version 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Veibel, S. (1972). *Acta Chem. Scand.* pp. 3685–3690.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

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12-(*N*-Benzoylimino)-11,12-dihydrobenzimidazo[2,1-*b*][1,3,5]benzothiadiazepine

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Abstract

The title compound, $C_{21}H_{14}N_4OS$, was prepared from the reaction of *N*-[2-(1*H*-benzimidazol-2-ylthio)phenyl]-*N*′-benzoylthiourea with dicyclohexylcarbodiimide. A puckered seven-membered ring and a short H$\cdots$H contact between two rings cause the whole molecule to be non-coplanar, even though the delocalized π-bonding system is planar. There is an intramolecular hydrogen bond between the amine H atom and the O atom of the carbonyl group.

Comment

The 1,3,5-thiadiazepines have received a great deal of interest because of their biological activities (Vecchia, Dellureficio, Kisis & Vlattas, 1983). As part of our program to develop new 1,3,5-thiadiazepine derivatives, we previously reported that the reaction of *N*-[2-(1*H*-benzimidazol-2-ylthio)phenyl]thiourea with dicyclohexylcarbodiimide (DCC) produced the unexpected 2-imino-3-(6-methoxybenzimidazol-2-yl)benzothiazoline *via* an intermolecular Smiles-type rearrangement (Song, Jin & Jeong, 1996). In contrast, the *N*-benzoylated compound, *N*′-benzoyl-*N*-[2-(1*H*-benzimidazol-2-ylthio)phenyl]thiourea, was cyclized to