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Novel *N*-Acyl α-Azidopyrrolidines (*N*-Acyliminium-Ion Precursors)

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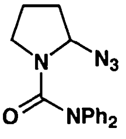
Abstract

As an alternative to the electrochemical procedure [Shono (1984). *Tetrahedron*, **40**, 811–850], *N*-acyliminium-ion precursors may be generated utilizing novel hypervalent iodine chemistry. The crystal structures of 2-azido-*N*,*N*-diphenylpyrrolidine-1-carboxamide, $C_{17}H_{17}N_5O$, and 2,5-diazido-*N*-(3,4,5-trimethoxybenzoyl)pyrrolidine, $C_{14}H_{17}N_7O_4$, are reported. In both instances the pyrrolidine ring is found in the half-chair conformation. The azido groups are non-linear with an average bond angle of 172.9 (1)°.

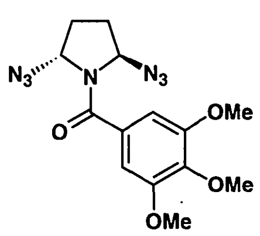
Comment

The oxidation of amides leading to the generation of *N*-acyliminium-ion precursors is a transformation which has broad synthetic utility. This reactive intermediate has found applications in many fields including alkaloid synthesis and lactam-based peptide mimetics (Hiemstra & Speckamp, 1988; Hart, 1988; Baldwin, Hulme, Edwards, Schofield & Parkes, 1993; Wong & Moeller, 1993). We have reported recently the oxidation of amides, carbamates and ureas using iodosobenzene $(PhIO)_n$ or *o*-iodosobenzoic acid with trimethylsilylazide ($TMSN_3$) in dichloromethane (Magnus, Hulme & Weber, 1994), to give *N*-acyliminium-ion precursors with an α-azido substituent (Clauss, Grimm & Prossel, 1974). Interestingly, there are no reports of crystal structures having the α-azidopyrrolidine moiety in the Cambridge Structural Database (1993).

The pyrrolidine rings each have the half-chair conformation in 2-azido-*N*,*N*-diphenylpyrrolidine-1-carboxamide, (I), and 2,5-diazido-*N*-(3,4,5-trimethoxybenzoyl)pyrrolidine, (II). The azido groups are decidedly non-linear. The angle at the central N atom of the azide group in (I) is 171.7 (2)° and those in (II) are 173.9 (3) and 173.1 (3)°. For (I), the geometry around the pyrrolidinic N atom is slightly pyramidalized with N1 being 0.132 (2) Å from the plane through C2, C5 and C9. The carbonyl-C9-to-N-atom bond length is slightly shorter for the pyrrolidinic N atom [1.369 (3) Å] than for the amino N atom [1.403 (2) Å].



(I)



(II) ,

For (II), N1 is only 0.041 (2) Å from the plane through C2, C5 and C12, and the carbonyl group (N1, C12, O13, C14) is nearly orthogonal to the phenyl ring (C15–C19) forming a dihedral angle of 69.0 (1)°. The carbonyl-to-phenyl-ring C—C bond length is

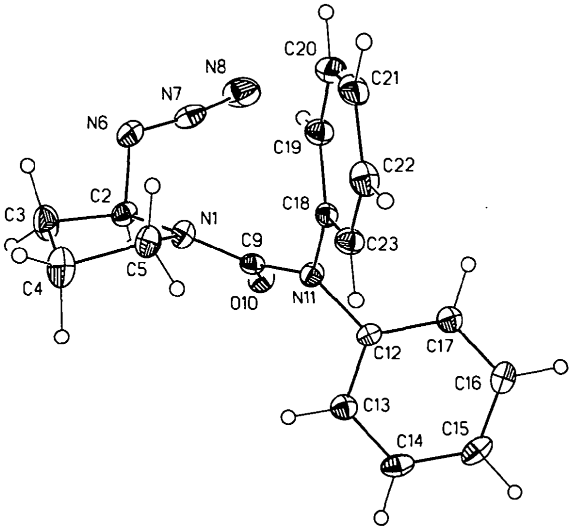


Fig. 1. Displacement ellipsoid plot of (I) showing the atom-labeling scheme; ellipsoids are scaled to the 30% probability level. H atoms are represented as spheres of arbitrary radii.

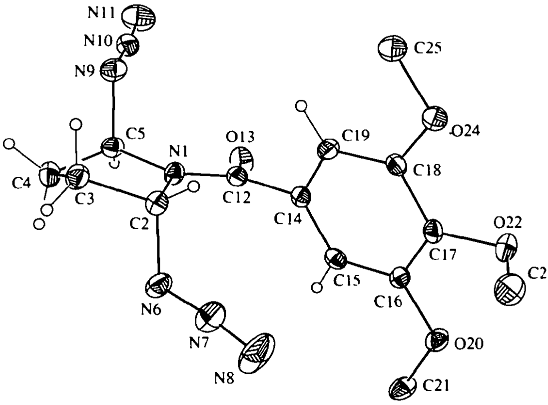


Fig. 2. Displacement ellipsoid plot of (II) showing the atom-labeling scheme; ellipsoids are scaled to the 30% probability level. H atoms are represented as spheres of arbitrary radii.

1.502 (3) Å. This fairly long C_{sp^2}—C_{sp^2} bond is probably the result of the non-conjugated nature of the interaction. The C—O bond lengths around the phenyl ring are shorter when the methoxy group is *meta* to the carbonyl group [average 1.359 (2) Å], than when it is *para* [1.383 (3) Å].

Experimental

Compound (I) was prepared by addition of trimethylsilylazide (TMSN$_3$) (4.8 eq.) to a suspension of iodosobenzene (2.4 eq.) in dichloromethane at 233 K, which turned yellow. *N*,*N*-Diphenylcarbamoylpyrrolidine (1 eq.) was added to the suspension which was stirred overnight at 233 K. (I) was produced in good yield (80%) forming X-ray quality crystals on slow evaporation of a dichloromethane–diethyl ether solution. At 233 K, the *trans* diazido product (II) predominated as a by-product in the oxidation of 3,4,5-trimethoxybenzoylpyrrolidine (5%). A similar diazide by-product was observed on the oxidation of *N*,*N*-diphenylcarbamoylpyrrolidine. However, this diazide was not crystalline.

Compound (I)

Crystal data

$C_{17}H_{17}N_5O$
$M_r = 307.35$
Monoclinic
$P2_1/c$
$a = 10.026\ (4)$ Å
$b = 9.230\ (3)$ Å
$c = 16.943\ (7)$ Å
$\beta = 97.30\ (3)°$
$V = 1555.2\ (10)$ Å^3
$Z = 4$
$D_x = 1.31$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 8.8$–$12.05°$
$\mu = 0.081$ mm^{-1}
$T = 173\ (1)$ K
Block
0.52 × 0.35 × 0.27 mm
Colorless

Data collection

Nicolet *R*3 diffractometer
ω scans (range 1.6°; 5–12° min^{-1})
Absorption correction: none
7762 measured reflections
3551 independent reflections
2331 observed reflections [$F > 4.0\sigma(F)$]

$R_{\rm int} = 0.020$
$\theta_{\rm max} = 27.5°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -22 \rightarrow 22$
4 standard reflections monitored every 96 reflections intensity decay: 1.3%

Refinement

Refinement on *F*
$R = 0.0489$
$wR = 0.0499$
$S = 1.329$
2331 reflections
276 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ 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) *for* (I)

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

	x	y	z	$U_{\rm eq}$
N1	0.2937 (2)	−0.4524 (2)	1.24896 (10)	0.0297 (5)
C2	0.2271 (2)	−0.5630 (3)	1.29072 (12)	0.0326 (7)
C3	0.2040 (3)	−0.4937 (3)	1.3695 (2)	0.0480 (9)
C4	0.2867 (3)	−0.3562 (3)	1.3761 (2)	0.0511 (10)
C5	0.2915 (3)	−0.3112 (2)	1.28994 (13)	0.0345 (8)
N6	0.0925 (2)	−0.6027 (2)	1.24834 (12)	0.0459 (7)
N7	0.0905 (2)	−0.6468 (2)	1.17968 (13)	0.0404 (7)
N8	0.0728 (2)	−0.6826 (3)	1.1150 (2)	0.0668 (10)
C9	0.3769 (2)	−0.4919 (2)	1.19457 (11)	0.0261 (6)
O10	0.40832 (14)	−0.6177 (2)	1.18424 (8)	0.0327 (5)
N11	0.4238 (2)	−0.3771 (2)	1.15135 (10)	0.0277 (5)
C12	0.5518 (2)	−0.3915 (2)	1.12278 (12)	0.0253 (6)
C13	0.6622 (2)	−0.4360 (2)	1.17462 (13)	0.0317 (7)
C14	0.7873 (2)	−0.4479 (3)	1.1483 (2)	0.0382 (7)
C15	0.8022 (2)	−0.4142 (2)	1.0700 (2)	0.0395 (8)
C16	0.6925 (2)	−0.3689 (2)	1.01869 (14)	0.0375 (8)
C17	0.5667 (2)	−0.3568 (2)	1.04472 (12)	0.0308 (7)
C18	0.3379 (2)	−0.2585 (2)	1.12381 (11)	0.0250 (6)
C19	0.2044 (2)	−0.2822 (3)	1.09426 (13)	0.0340 (7)
C20	0.1214 (3)	−0.1657 (3)	1.07083 (14)	0.0394 (8)
C21	0.1717 (3)	−0.0266 (3)	1.07454 (13)	0.0386 (8)
C22	0.3058 (3)	−0.0028 (3)	1.10202 (13)	0.0362 (7)
C23	0.3889 (2)	−0.1186 (2)	1.12716 (13)	0.0313 (7)

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

C2—N1	1.453 (3)	C13—C12	1.385 (3)
C5—N1	1.478 (3)	C17—C12	1.387 (3)
C9—N1	1.369 (3)	C14—C13	1.388 (3)
C3—C2	1.523 (4)	C15—C14	1.389 (4)
N6—C2	1.491 (3)	C16—C15	1.378 (3)
C4—C3	1.513 (4)	C17—C16	1.392 (3)
C5—C4	1.525 (4)	C19—C18	1.386 (3)
N7—N6	1.230 (3)	C23—C18	1.387 (3)
N8—N7	1.136 (3)	C20—C19	1.386 (3)
O10—C9	1.222 (2)	C21—C20	1.378 (3)
N11—C9	1.403 (3)	C22—C21	1.384 (3)
C12—N11	1.435 (3)	C23—C22	1.388 (3)
C18—N11	1.434 (2)		
C2—N1—C5	110.8 (2)	C13—C12—C17	119.9 (2)
C2—N1—C9	119.9 (2)	C13—C12—N11	119.4 (2)
C5—N1—C9	126.7 (2)	C17—C12—N11	120.6 (2)
C3—C2—N6	107.2 (2)	C14—C13—C12	120.1 (2)
C3—C2—N1	105.2 (2)	C15—C14—C13	120.1 (2)
N6—C2—N1	112.5 (2)	C16—C15—C14	119.7 (2)
C4—C3—C2	105.9 (2)	C17—C16—C15	120.5 (2)
C5—C4—C3	103.9 (2)	C12—C17—C16	119.7 (2)
N1—C5—C4	102.4 (2)	C19—C18—C23	119.7 (2)
N7—N6—C2	116.2 (2)	C19—C18—N11	120.6 (2)
N8—N7—N6	171.7 (2)	C23—C18—N11	119.6 (2)
O10—C9—N11	122.3 (2)	C20—C19—C18	119.8 (2)
O10—C9—N1	122.7 (2)	C21—C20—C19	120.5 (2)
N11—C9—N1	115.0 (2)	C22—C21—C20	119.8 (2)
C12—N11—C18	119.2 (2)	C23—C22—C21	120.0 (2)
C12—N11—C9	118.6 (2)	C18—C23—C22	120.0 (2)
C18—N11—C9	121.3 (2)		

Compound (II)

Crystal data

$C_{14}H_{17}N_7O_4$
$M_r = 347.33$
Monoclinic
$P2_1/c$
$a = 10.198\ (2)$ Å
$b = 18.087\ (3)$ Å
$c = 10.232\ (2)$ Å
$\beta = 119.77\ (1)°$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 6.0$–$12.1°$
$\mu = 0.100$ mm^{-1}
$T = 173\ (1)$ K
Block

$V = 1638.2\ (6)\ Å^3$
$Z = 4$
$D_x = 1.41\ \mathrm{Mg\ m^{-3}}$

$0.52 \times 0.21 \times 0.17$ mm
Colorless

Data collection

Nicolet *R*3 diffractometer
ω scans (range 1.2°; 3–6° $\mathrm{min^{-1}}$)
Absorption correction: none
3051 measured reflections
2879 independent reflections
1914 observed reflections [$F > 4.0\sigma(F)$]

$R_{\mathrm{int}} = 0.012$
$\theta_{\mathrm{max}} = 25.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 21$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 97 reflections intensity decay: 1.5%

Refinement

Refinement on *F*
$R = 0.040$
$wR = 0.041$
$S = 1.213$
1914 reflections
295 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\mathrm{max}} = 0.04$

$\Delta\rho_{\mathrm{max}} = 0.18\ \mathrm{e\ Å^{-3}}$
$\Delta\rho_{\mathrm{min}} = -0.19\ \mathrm{e\ Å^{-3}}$
Extinction correction: modified Larson (*SHELXTL-Plus*; Sheldrick, 1991)
Extinction coefficient: $3.0\ (4) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for* (II)

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

	x	y	z	U_{eq}
N1	0.3893 (2)	0.71746 (10)	0.3038 (2)	0.0276 (9)
C2	0.4041 (3)	0.64083 (13)	0.2673 (3)	0.0286 (12)
C3	0.5411 (3)	0.6431 (2)	0.2474 (3)	0.0352 (13)
C4	0.6375 (3)	0.7036 (2)	0.3548 (3)	0.0393 (13)
C5	0.5221 (3)	0.76169 (13)	0.3378 (3)	0.0307 (11)
N6	0.4335 (2)	0.59211 (11)	0.3964 (3)	0.0385 (11)
N7	0.3308 (3)	0.54766 (12)	0.3696 (3)	0.0478 (14)
N8	0.2449 (3)	0.50520 (14)	0.3581 (4)	0.077 (2)
N9	0.4863 (2)	0.80972 (11)	0.2061 (2)	0.0371 (11)
N10	0.4728 (2)	0.87591 (13)	0.2250 (2)	0.0363 (11)
N11	0.4587 (3)	0.93755 (13)	0.2284 (3)	0.0581 (14)
C12	0.2740 (3)	0.74558 (13)	0.3192 (3)	0.0270 (11)
O13	0.2785 (2)	0.80767 (9)	0.3685 (2)	0.0394 (9)
C14	0.1358 (3)	0.69782 (12)	0.2620 (3)	0.0249 (10)
C15	0.0934 (3)	0.66871 (13)	0.3608 (3)	0.0263 (11)
C16	−0.0381 (3)	0.62663 (12)	0.3041 (3)	0.0256 (11)
C17	−0.1281 (3)	0.61689 (12)	0.1495 (3)	0.0261 (11)
C18	−0.0834 (3)	0.64571 (12)	0.0513 (3)	0.0261 (11)
C19	0.0494 (3)	0.68584 (13)	0.1086 (3)	0.0277 (11)
O20	−0.0882 (2)	0.59303 (9)	0.3901 (2)	0.0333 (8)
C21	0.0088 (4)	0.5947 (2)	0.5487 (3)	0.0402 (15)
O22	−0.2641 (2)	0.57972 (9)	0.0921 (2)	0.0347 (8)
C23	−0.2556 (4)	0.5029 (2)	0.0659 (4)	0.048 (2)
O24	−0.1776 (2)	0.63160 (9)	−0.0969 (2)	0.0340 (8)
C25	−0.1268 (4)	0.6531 (2)	−0.1991 (3)	0.0367 (14)

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

C2—N1	1.462 (3)	C14—C12	1.502 (3)
C5—N1	1.459 (3)	C15—C14	1.385 (4)
C12—N1	1.360 (4)	C19—C14	1.384 (3)
C3—C2	1.509 (5)	C16—C15	1.393 (3)
N6—C2	1.489 (4)	C17—C16	1.391 (3)
C4—C3	1.516 (4)	O20—C16	1.361 (4)
C5—C4	1.521 (4)	C18—C17	1.394 (4)
N9—C5	1.488 (4)	O22—C17	1.383 (3)
N7—N6	1.238 (3)	C19—C18	1.385 (3)
N8—N7	1.127 (4)	O24—C18	1.357 (2)
N10—N9	1.231 (3)	C21—O20	1.421 (3)
N11—N10	1.127 (3)	C23—O22	1.427 (3)
O13—C12	1.223 (3)	C25—O24	1.433 (5)
C2—N1—C5	112.3 (2)	C15—C14—C19	121.0 (2)
C2—N1—C12	126.0 (2)	C15—C14—C12	120.5 (2)
C5—N1—C12	121.4 (2)	C19—C14—C12	118.5 (3)
C3—C2—N6	110.1 (2)	C16—C15—C14	119.2 (2)
C3—C2—N1	103.2 (2)	C17—C16—O20	115.6 (2)
N6—C2—N1	109.6 (2)	C17—C16—C15	119.8 (3)
C4—C3—C2	103.4 (3)	O20—C16—C15	124.6 (2)
C5—C4—C3	103.3 (2)	C18—C17—O22	119.6 (2)
N9—C5—N1	108.8 (2)	C18—C17—C16	120.4 (2)
N9—C5—C4	109.6 (3)	O22—C17—C16	120.0 (3)
N1—C5—C4	102.8 (2)	C19—C18—O24	124.9 (3)
N7—N6—C2	114.3 (2)	C19—C18—C17	119.5 (2)
N8—N7—N6	173.9 (3)	O24—C18—C17	115.6 (2)
N10—N9—C5	115.0 (2)	C14—C19—C18	120.0 (3)
N11—N10—N9	173.1 (3)	C21—O20—C16	117.2 (2)
O13—C12—C14	121.6 (2)	C23—O22—C17	114.3 (2)
O13—C12—N1	122.3 (2)	C25—O24—C18	116.9 (2)
C14—C12—N1	116.0 (2)		

Crystals of compound (II) have nearly hexagonal metric symmetry. The *R* value for merging equivalent reflections in the hexagonal space group *P*6(3) was 0.47 for 1468 'unique' reflections.

Data collection: *P3/V Data Collection System* (Siemens, 1989). Cell refinement: *P3/V Data Collection System*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *MPLN* (Cordes, 1983), *FUER* (Larson, 1982), *PLATON*92 (Spek, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,6-Dimethyl-2-(4-nitrobenzylidene)-3(2*H*)-benzofuranone

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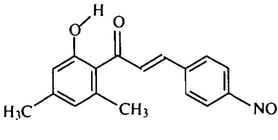
Abstract

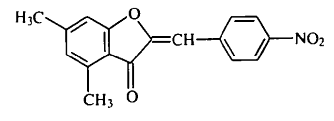
The crystal structure of the title compound, $C_{17}H_{13}NO_4$, is stabilized by both intra- and intermolecular C—H···O hydrogen bonds, and also by $\pi\cdots\pi$ interactions.

Comment

We have found that some 2′-hydroxy-4′,6′-dimethylchalcones undergo solid-state Michael reactions to yield the corresponding flavanones. In connection with this, we attempted to synthesize various chalcone derivatives to examine their solid-state reactivities (Goud, Panneerselvam, Zacharias & Desiraju, 1995). The literature procedure for the synthesis of these chalcones involves treatment of 2-hydroxy-3,5-dimethylacetophenone with the corresponding substituted benzaldehydes in a basic medium. However, when this procedure was attempted with 4-nitrobenzaldehyde [using the recommended $Ba(OH)_2$ rather than NaOH; Matsuoka & Fujise, 1957], the product was not the expected 2′-hydroxy-4′,6′-dimethyl-4-nitrochalcone, (1), but instead the oxidation product aurone, (2). In general, aurones can serve as convenient precursors to flavonoid-type natural products (Adam, Hadjiarapoglou & Levai, 1992); therefore, we solved the crystal structure of (2) to examine the structural aspects.



(1)



(2)

Fig. 1 shows aurone (2) with the atomic numbering scheme. There are two molecules in the asymmetric unit. The double bond of the aurone has a *Z* configuration. Both molecules in the asymmetric unit are planar and this planar geometry is possibly stabilized by intramolecular C—H···O hydrogen bonding (C5···O3, H5···O3 and C5—H5···O3 are 2.93, 2.28 Å and 126°, respectively, in molecule *A*, and 2.98, 2.28 Å and 127°, respectively, in molecule *B*). The crystal structure of (2) is stabilized additionally by extensive intermolecular C—H···O hydrogen bonds, $\pi\cdots\pi$

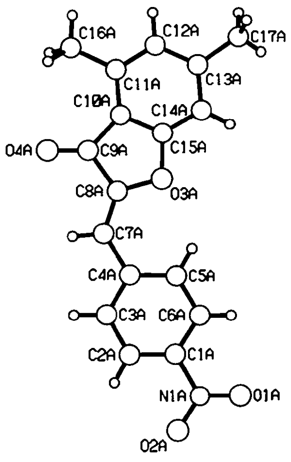


Fig. 1. Atomic numbering scheme for molecule *A* of aurone (2). The numbering for molecule *B* is identical.

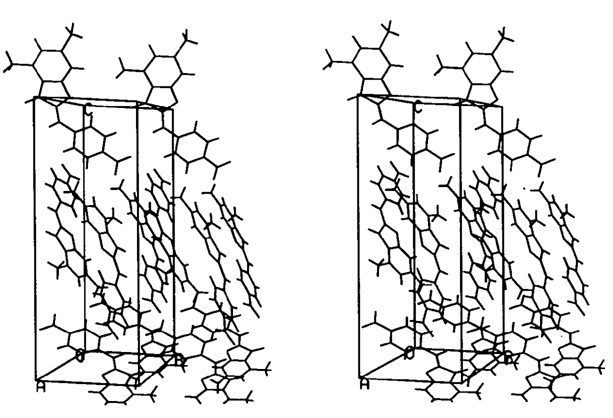


Fig. 2. Packing diagram of (2) showing inversion-related molecules.

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