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Structures of 1,1'-Diphenyl-1,1'-bicyclopentyl, 1,1'-Diphenyl-1,1'-bicyclohexyl and 1,1'-Diphenyl-1,1'-bicycloheptyl

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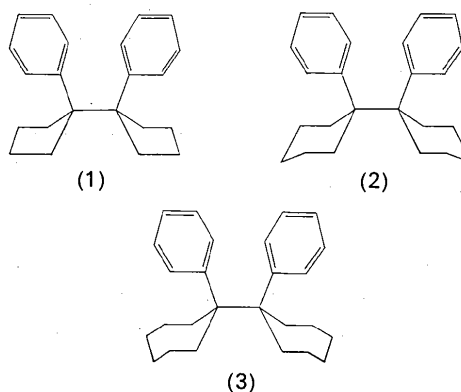
Abstract

Of the title compounds, 1,1'-diphenyl-1,1'-bicyclopentyl, $C_{22}H_{26}$ (1), 1,1'-diphenyl-1,1'-bicyclohexyl, $C_{24}H_{30}$ (2) and 1,1'-diphenyl-1,1'-bicycloheptyl $C_{26}H_{34}$ (3), (1) adopts the *gauche* conformation whereas (2) and (3) are in the *trans* conformation. The cyclopentyl ring is in envelope form and the cyclohexyl ring in chair form, while the cycloheptyl ring is in a twisted-chair configuration. The influence of increasing ring size on the central inter-ring C—C bond length is discussed as well as the effects of steric interaction within the molecules.

Comment

Sterically congested diphenylethane derivatives in which the central C—C bond is elongated have stimulated much interest, both from the point of view of providing data for the calibration of force-field parameters and with regard to structure-reactivity relationships (Maslak, Narvaez & Parvez, 1991, and references cited therein). During a study of the relationship between thermal stability, strain and structure in a series of 1,1'-diphenyl-1,1'-bicycloalkyls (C_4 – C_8), Bernlöhner, Beckhaus, Lindner & Rüdhardt (1984) determined the crystal structure of 1,1'-diphenyl-1,1'-bicyclooctyl and found it to have a *trans* conformation. Using MM2 calculations, they concluded that the bicyclo-heptyl and -hexyl compounds would also have the *trans* conformation but that the -pentyl compound would have a *gauche* conformation. These conclusions have yet to be confirmed experimentally. In view of our interest in diphenylethane derivatives and the possibility of synthesizing some of the 1,1'-diphenyl-1,1'-bicycloalkyl compounds with greater ease through the agency of the *tert*-butyloxy free radical than through electrochemical means, we decided to investigate the structures of other members of the 1,1'-diphenyl-1,1'-bicycloalkyl family of compounds to provide the experimental structural data which had hitherto been

lacking. This paper reports the single crystal X-ray data for the title compounds (1), (2) and (3).



Compound (1) crystallizes in the tetragonal space group $I4_1/a$. The molecular structure is shown in Fig. 1 and geometrical parameters are given in Table 2. The molecule as a whole adopts a *gauche* conformation, like 1,1'-dinitrobicyclopentyl (Lam, Huang & Hambley, 1990) but unlike 1,1'-dicyanobicyclopentyl which has a *trans* structure (Koh, Huang & Sim, 1992). There is a twofold rotational axis through the centre of the central C(1)—C(1A) bond so that the asymmetric and crystallographically independent unit is just half of the molecule. The cyclopentyl ring adopts the envelope form. The torsion angle between bonds C(2)—C(3) and C(4)—C(5) is only -3.4° , so that the four atoms C(2), C(3), C(4) and C(5) are essentially coplanar.

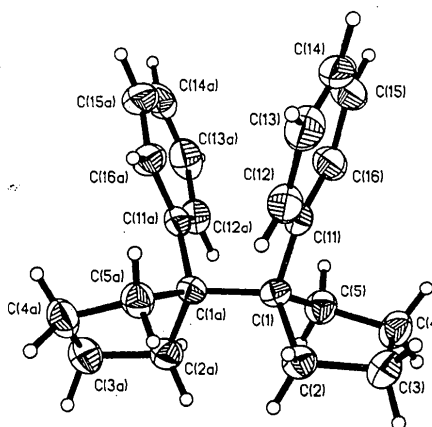


Fig. 1. ORTEP (Johnson, 1965) plot of 1,1'-diphenyl-1,1'-bicyclopentyl (1).

The central C(1)—C(1A) bond is 1.575 (7) Å, slightly longer than the analogous bond in 1,1'-dicyanobicyclopentyl [1.537 (5) Å; Koh, Huang & Sim, 1992] and in 1,1'-dinitrobicyclopentyl [1.486 (4) Å; Lam, Huang & Hambley, 1990].

Apart from the long central C(1)—C(1A) bond, the bond angles around the two central C atoms also reveal evidence of intramolecular stress. Thus, within the cyclopentyl ring, the bond angle C(2)—C(1)—C(5) [98.9 (3) $^\circ$] is noticeably smaller than the other four angles (105.0–105.9 $^\circ$). Moreover, the angle C(12)—C(11)—C(16) within the phenyl group is also strained [116.4 (4) $^\circ$] showing the largest deviation from 120 $^\circ$ of any of the internal phenyl-ring angles. The phenyl ring is planar with a mean deviation from planarity of 0.0025 Å.

Compound (2) crystallizes in the monoclinic space group $C2/c$. The molecule is centrosymmetric (Fig. 2, Table 2) with the symmetry centre in the middle of the central C(1)—C(1A) bond. The molecule adopts a *trans* conformation like 1,1'-dicyano-1,1'-bicyclohexyl (Koh, Huang & Sim, 1992) but in contrast to the *gauche* conformation of 1,1'-dinitro-1,1'-bicyclohexyl (Lam, Huang & Hambley, 1990). The cyclohexyl ring forms a perfect chair with C(2), C(3), C(5) and C(6) coplanar (the mean deviation from planarity is only 0.0023 Å).

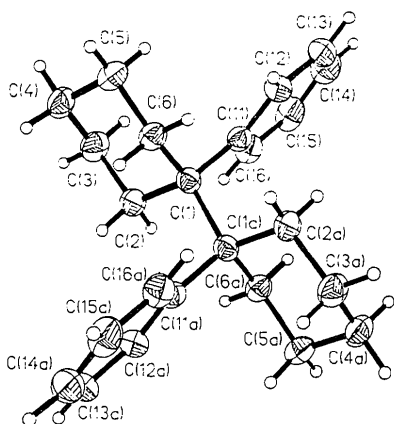


Fig. 2. ORTEP plot of 1,1'-diphenyl-1,1'-bicyclohexyl (2).

The central C(1)—C(1A) bond in (2) is extremely long [1.627 (5) Å], much longer than in 1,1'-dicyano-1,1'-bicyclohexyl [1.582 (10) Å; Koh, Huang & Sim, 1992] or 1,1'-dinitro-1,1'-bicyclohexyl [1.579 (3) Å]. This can be explained again by the intramolecular steric repulsion between the phenyl and cyclohexyl groups and the steric strain around the C(1)—C(1A) bond. The bond angles around the central bond also reflect the steric strain. Within the cyclohexyl ring, the angle C(2)—C(1)—C(6) [compressed to a value of 105.5 (2) $^\circ$] is significantly smaller than the other internal ring angles whose values range from 110.8 to 113.6 $^\circ$. In the phenyl group, the angle C(12)—C(11)—C(16) is only 116.1 (3) $^\circ$, compared with 119.6–122.2 $^\circ$ for the other phenyl-ring angles. The phenyl ring in (2) is essentially planar with a mean deviation from planarity of 0.0026 Å.

Compound (3) crystallizes in the same space group as (2). There are three crystallographically different molecules in the unit cell (see Fig. 3, Table 2): molecule (I) has a slightly lower symmetry than molecules (II) and (III) which both have a twofold symmetry axis through the middle of the central C(1)—C(1A) bond. The crystal of (3) is less well packed than that of (2), as revealed by its lower density (1.137 compared with 1.160 Mg m $^{-3}$). All three molecules adopt a *trans* conformation. The bond lengths, bond angles and torsion angles in the three molecules are very similar (see Table 2). This indicates that, despite the need to adjust to the crystal-lattice environment, the *trans* conformation is basically more stable than the *gauche*. The two phenyl rings in (3) are nearly parallel, being tilted by 4 $^\circ$. The cycloheptyl ring is in a twisted-chair form. If a plane is fitted through one of the cycloheptyl rings, C(1), C(2), C(3), C(4), C(5), C(6) and C(7), then C(2), C(4) and C(6) lie above the plane and C(1), C(3), C(5) and C(7) below, with deviations of up to 0.5 Å. The phenyl ring is also strained with a C(12)—C(11)—C(16) angle of 116.5 (5) $^\circ$ which is comparable to the corresponding angles in the bicyclohexyl and bicyclopentyl compounds. This strain also results in an average mean deviation from planarity of 0.013 Å, greater than in (1) or (2). The central bond lengths in the three crystallographically independent molecules are: C(1)—C(1A) 1.630 (8), C(21)—C(21A) 1.627 (11) and C(41)—C(41A)

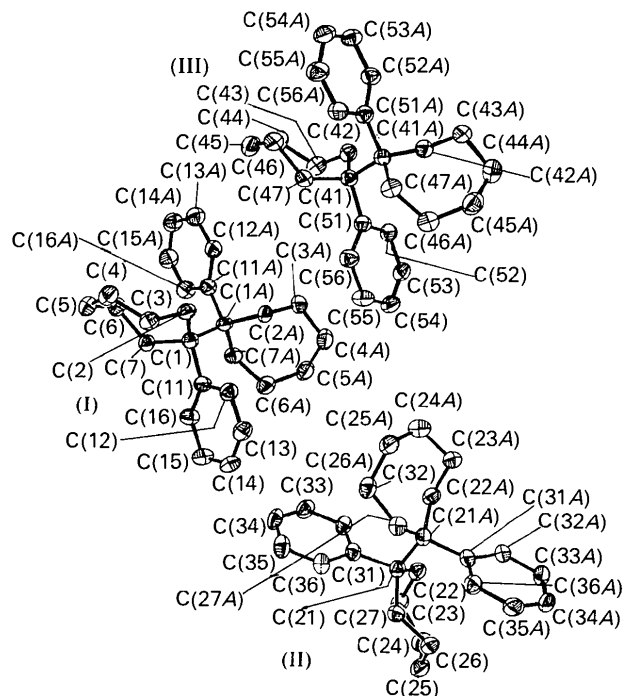


Fig. 3. ORTEP plot of 1,1'-diphenyl-1,1'-bicycloheptyl (3).

1.633 (12) Å. With an average value of 1.630 Å, this provides another example of an elongated central C—C bond within a sterically congested diphenylethane derivative (Rüchardt & Beckhaus, 1980; Maslak, Narvaez & Parvez, 1991).

Table 3 summarizes the central C—C bond lengths in various 1,1'-(*R*)(*R*)-1,1'-bicycloalkyl (*R* = nitro, cyano or phenyl) compounds (obtained from single-crystal structure determinations). From the variation in the central C—C bond lengths listed in Table 3, it is clear that as the crowding around the two central C atoms increases, the central inter-ring C—C bond length also increases. However, when the carbocyclic ring is sufficiently large, further increase in the central C—C bond length is no longer significant. This point is reached by about C₇ when overcrowding is at a maximum. For this series of compounds, it would appear that the central C—C bond length reaches its upper limit at around 1.63–1.64 Å. However, this is still a little shorter than the longest ethane central C—C bond length observed so far (1.67 Å; see Maslak, Narvaez & Parvez, 1991).

Table 3 also gives the values of the carbocyclic ring angle at one of the central C atoms defined by C(2)—C(1)—C(*n*) (where *n* = 5–7) for the compounds represented by 1,1'-(*R*)(*R*)-1,1'-bicycloalkyl. It can be seen that for the 1,1'-diphenyl-1,1'-bicycloalkyl series, this angle is invariably smaller than the tetrahedral angle with the greatest contraction occurring in the cyclopentyl compound. Replacing the phenyl rings by cyano groups causes this angle to widen relative to the 1,1'-diphenyl-1,1'-bicycloalkyl series. This widening is further increased with nitro substitution. For *n* = 5, the smallest deviation from the tetrahedral angle (109.5°) is observed in 1,1'-dinitro-1,1'-bicyclopentyl (105.4°). For *n* = 7, the deviation is greatest in 1,1'-dinitro-1,1'-bicycloheptyl with an angle of 113.2°. The deviations for the cyclohexyl nitro and cyano compounds are relatively small.

Bernlöhr, Beckhaus, Lindner & Rüchardt (1984) have calculated the energies of the rotamers for some 1,1'-diphenyl-1,1'-bicycloalkyl compounds (*n* = 4–8) using an empiric force field (EFF) combined with an MM2 force field (although no details are given in their paper). Our X-ray results presented here are consistent with the conclusions of their MM2 calculations that the *gauche* conformer is more stable than the *trans* in (1) and that the *trans* is more stable than the *gauche* in (2) and (3). We have also carried out semi-empirical molecular-orbital calculations to determine the relative energies of the *gauche* and *trans* rotamers for all three compounds using AMPAC with AM1 parametrization and allowing full geometry optimization starting from the experimental solid-state molecular structures (Tan, Lam, Huang & Chia, 1990). Fig. 4 shows the variation of

the energy of 1,1'-diphenyl-1,1'-bicyclopentyl as a function of the C(2)—C(1)—C(1A)—C(2A) torsion angle. The energy differences between the *gauche* and *trans* conformations ($\Delta E = E_g - E_t$) are -7.65 and 6.37 in compounds (1) and (2); and -2.73 and 3.58 in compound (3). The *gauche* populations are 97.8, 13.3 and 76.5% in (1), (2) and (3), respectively.

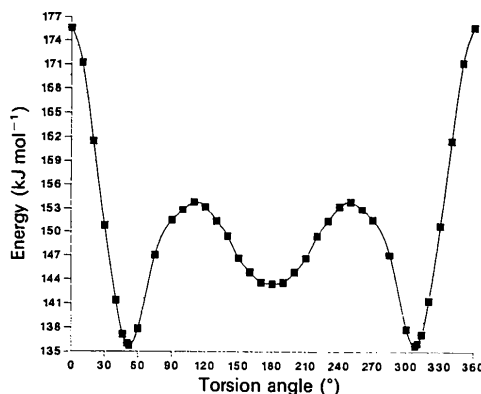


Fig. 4. Energy of 1,1'-diphenyl-1,1'-bicyclopentyl as a function of the central torsional angle, determined by AM1 calculations.

It can be seen that while AM1 parametrization predicts correctly the most stable bicyclopentyl conformation to be *gauche* and the most stable bicyclohexyl conformation to be *trans*, the prediction for the bicycloheptyl conformation suggests that both *trans* and *gauche* have approximately equal energies. It is possible that the probable errors (up to 5 kJ mol⁻¹) in the AM1 method are such that, for the larger bicycloheptyl compound, the calculated results are less reliable. Furthermore, these calculations are for isolated molecules whose preferred conformations may differ from those imposed by the solid state.

Experimental

Compound (1)

Crystal data

C₂₂H₂₆
M_r = 290.4
 Tetragonal
 I4₁/a (origin at $\bar{1}$)
a = 10.2050 (10) Å
c = 32.229 (10) Å
V = 3356.6 (11) Å³
Z = 8
D_x = 1.149 Mg m⁻³

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 4.865–14.8°
 μ = 0.060 mm⁻¹
T = 297 K
 Prism
 0.4 × 0.25 × 0.25 mm
 Colourless

Data collection

Siemens R3m/V diffractometer

*R*_{int} = 0.0336
 θ_{\max} = 25.0°

ω scans
Absorption correction:
none
1666 measured reflections
1489 independent reflections
645 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F
Final $R = 0.599$
 $wR = 0.485$
 $S = 1.53$
645 reflections
101 parameters
H-atom parameters not refined

Compound (2)*Crystal data*

$C_{24}H_{30}$
 $M_r = 318.5$
Monoclinic
 $C2/c$
 $a = 17.306$ (9) Å
 $b = 6.499$ (3) Å
 $c = 16.596$ (11) Å
 $\beta = 102.29$ (5)°
 $V = 1824$ (2) Å³
 $Z = 4$

Data collection

Siemens $R3m/V$ diffractometer
 ω scans
Absorption correction:
none
1664 measured reflections
1609 independent reflections
656 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F
Final $R = 0.0368$
 $wR = 0.0438$
 $S = 0.64$
656 reflections
110 parameters
H-atom parameters not refined

Compound (3)*Crystal data*

$C_{26}H_{34}$
 $M_r = 346.5$

$h = 0 \rightarrow 12$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 37$
2 standard reflections
monitored every 98
reflections
intensity variation: $\pm 1.5\%$

$w = 1/[\sigma^2(F) + 0.0001F^2]$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.16$ e Å⁻³
 $\Delta\rho_{\min} = -0.17$ e Å⁻³
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

$D_x = 1.160$ Mg m⁻³
Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
Cell parameters from 17
reflections
 $\theta = 3.48$ – 9.925°
 $\mu = 0.065$ mm⁻¹
 $T = 298$ K
Plate
 $0.4 \times 0.4 \times 0.05$ mm
Colourless

$R_{\text{int}} = 0.0157$
 $\theta_{\max} = 25.0^\circ$
 $h = 0 \rightarrow 20$
 $k = 0 \rightarrow 7$
 $l = -19 \rightarrow 18$
3 standard reflections
monitored every 97
reflections
intensity variation: $\pm 1.5\%$

$w = 1/[\sigma^2(F) + 0.0023F^2]$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.12$ e Å⁻³
 $\Delta\rho_{\min} = -0.10$ e Å⁻³
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Monoclinic
 $C2/c$
 $a = 20.841$ (13) Å
 $b = 20.805$ (16) Å
 $c = 19.27$ (2) Å
 $\beta = 104.25$ (6)°
 $V = 8097$ (11) Å³
 $Z = 16$
 $D_x = 1.137$ Mg m⁻³

Data collection

Siemens $R3m/V$ diffractometer
 ω scans
Absorption correction:
none
6323 measured reflections
6139 independent reflections
2600 observed reflections
 $[I > 2.5\sigma(I)]$

Refinement

Refinement on F
Final $R = 0.0713$
 $wR = 0.0890$
 $S = 1.04$
2600 reflections
470 parameters
H-atom parameters not refined

Cell parameters from 18
reflections
 $\theta = 3.17$ – 8.55°
 $\mu = 0.063$ mm⁻¹
 $T = 298$ K
Prism
 $0.4 \times 0.4 \times 0.4$ mm
Colourless

$R_{\text{int}} = 0.0226$
 $\theta_{\max} = 24.0^\circ$
 $h = 0 \rightarrow 23$
 $k = 0 \rightarrow 23$
 $l = -22 \rightarrow 21$
3 standard reflections
monitored every 97
reflections
intensity variation: $\pm 1.5\%$

$w = 1/[\sigma^2(F) + 0.0053F^2]$
 $(\Delta/\sigma)_{\max} = 0.000$
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(1)				
C(1)	0.4317 (3)	0.7859 (3)	0.3401 (1)	0.050 (1)
C(2)	0.4101 (4)	0.8782 (4)	0.3025 (1)	0.068 (2)
C(3)	0.2624 (4)	0.8993 (4)	0.3002 (1)	0.085 (2)
C(4)	0.2006 (4)	0.7810 (4)	0.3216 (1)	0.079 (2)
C(5)	0.3156 (4)	0.6922 (4)	0.3331 (1)	0.067 (2)
C(11)	0.4168 (4)	0.8637 (4)	0.3807 (1)	0.054 (2)
C(12)	0.4780 (4)	0.9837 (4)	0.3864 (1)	0.070 (2)
C(13)	0.4694 (5)	1.0496 (5)	0.4235 (2)	0.094 (2)
C(14)	0.4012 (6)	1.0004 (7)	0.4561 (2)	0.105 (3)
C(15)	0.3408 (5)	0.8823 (6)	0.4513 (2)	0.094 (2)
C(16)	0.3484 (4)	0.8141 (4)	0.4144 (1)	0.071 (2)
(2)				
C(1)	-0.2029 (2)	-0.2289 (5)	0.0047 (2)	0.038 (1)
C(2)	-0.1805 (2)	-0.0126 (5)	0.0407 (2)	0.045 (1)
C(3)	-0.0912 (2)	0.0307 (5)	0.0573 (2)	0.053 (1)
C(4)	-0.0456 (2)	-0.1274 (6)	0.1166 (2)	0.059 (1)
C(5)	-0.0656 (2)	-0.3441 (5)	0.0851 (2)	0.057 (1)
C(6)	-0.1549 (2)	-0.3816 (5)	0.0676 (2)	0.048 (1)
C(11)	-0.1805 (2)	-0.2516 (5)	-0.0801 (2)	0.042 (1)
C(12)	-0.1540 (2)	-0.4372 (5)	-0.1067 (2)	0.053 (1)
C(13)	-0.1339 (2)	-0.4565 (7)	-0.1830 (2)	0.069
C(14)	-0.1399 (2)	-0.2898 (6)	-0.2346 (2)	0.075 (2)
C(15)	-0.1664 (2)	-0.1042 (7)	-0.2112 (2)	0.064 (1)
C(16)	-0.1857 (2)	-0.0858 (5)	-0.1348 (2)	0.051 (1)
(3) Molecule (I)				
C(1)	0.3452 (2)	-0.1026 (3)	0.2384 (3)	0.044 (2)
C(2)	0.2727 (2)	-0.1225 (3)	0.2037 (3)	0.048 (2)
C(3)	0.2622 (3)	-0.1920 (3)	0.1779 (3)	0.056 (2)
C(4)	0.2604 (3)	-0.1989 (3)	0.0982 (3)	0.063 (2)

C(5)	0.3245 (3)	-0.1854 (3)	0.0770 (3)	0.062 (3)	(2)			
C(6)	0.3576 (3)	-0.1218 (3)	0.1045 (3)	0.054 (2)	C(1)—C(2)	1.545 (4)	C(1)—C(6)	1.550 (4)
C(7)	0.3882 (3)	-0.1217 (3)	0.1861 (3)	0.047 (2)	C(1)—C(11)	1.544 (4)	C(1)—C(1A)	1.627 (5)
C(11)	0.3715 (3)	-0.1400 (3)	0.3093 (3)	0.045 (2)	C(2)—C(3)	1.537 (4)	C(3)—C(4)	1.521 (5)
C(12)	0.3296 (3)	-0.1582 (3)	0.3529 (3)	0.051 (2)	C(4)—C(5)	1.516 (5)	C(5)—C(6)	1.529 (4)
C(13)	0.3583 (3)	-0.1873 (3)	0.4184 (3)	0.057 (2)	C(11)—C(12)	1.396 (5)	C(11)—C(16)	1.399 (5)
C(14)	0.4206 (3)	-0.2002 (3)	0.4430 (3)	0.061 (3)	C(12)—C(13)	1.388 (5)	C(13)—C(14)	1.371 (6)
C(15)	0.4625 (3)	-0.1853 (3)	0.3996 (3)	0.061 (2)	C(14)—C(15)	1.376 (6)	C(15)—C(16)	1.384 (5)
C(16)	0.4374 (3)	-0.1557 (3)	0.3338 (3)	0.053 (2)	C(2)—C(1)—C(6)	105.5 (2)	C(2)—C(1)—C(11)	110.4 (3)
C(1A)	0.3503 (3)	-0.0258 (3)	0.2551 (3)	0.045 (2)	C(6)—C(1)—C(11)	110.5 (2)	C(2)—C(1)—C(1A)	110.7 (3)
C(2A)	0.2974 (3)	-0.0050 (3)	0.2957 (3)	0.049 (2)	C(6)—C(1)—C(1A)	109.8 (3)	C(11)—C(1)—C(1A)	109.8 (2)
C(3A)	0.3038 (3)	0.0645 (3)	0.3232 (3)	0.058 (2)	C(1)—C(2)—C(3)	113.3 (2)	C(2)—C(3)—C(4)	110.8 (3)
C(4A)	0.3431 (3)	0.0704 (3)	0.4013 (3)	0.069 (3)	C(3)—C(4)—C(5)	110.8 (2)	C(4)—C(5)—C(6)	111.2 (3)
C(5A)	0.4162 (3)	0.0552 (3)	0.4162 (3)	0.070 (3)	C(1)—C(6)—C(5)	113.6 (3)	C(1)—C(11)—C(12)	122.3 (3)
C(6A)	0.4321 (3)	-0.0087 (3)	0.3850 (3)	0.060 (2)	C(1)—C(11)—C(16)	121.6 (3)	C(12)—C(11)—C(16)	116.1 (3)
C(7A)	0.4201 (3)	-0.0079 (3)	0.3036 (3)	0.049 (2)	C(11)—C(12)—C(13)	122.0 (3)	C(12)—C(13)—C(14)	119.9 (4)
C(11A)	0.3383 (3)	0.0111 (3)	0.1837 (3)	0.046 (2)	C(13)—C(14)—C(15)	120.2 (4)	C(14)—C(15)—C(16)	119.6 (4)
C(12A)	0.2757 (3)	0.0284 (3)	0.1442 (3)	0.052 (2)	C(11)—C(16)—C(15)	122.2 (3)		
C(13A)	0.2650 (3)	0.0568 (3)	0.0766 (3)	0.064 (3)				
C(14A)	0.3174 (4)	0.0695 (3)	0.0477 (3)	0.065 (3)	C(11)—C(1)—C(1A)—C(2A)			57.9 (2)
C(15A)	0.3807 (4)	0.0554 (3)	0.0859 (3)	0.065 (3)	C(11)—C(1)—C(1A)—C(6A)			-58.3 (2)
C(16A)	0.3909 (3)	0.0274 (3)	0.1526 (3)	0.057 (2)				

(3) Molecule (II)

C(21)	0.0401 (3)	0.2168 (2)	0.7570 (3)	0.045 (2)	C(1)—C(1A)	1.630 (8)	C(1)—C(7)	1.554 (8)
C(22)	0.0698 (3)	0.2797 (3)	0.7928 (3)	0.051 (2)	C(1)—C(11)	1.551 (7)	C(1A)—C(7A)	1.567 (7)
C(23)	0.1465 (3)	0.2825 (3)	0.8170 (3)	0.056 (2)	C(1A)—C(11A)	1.541 (8)	C(4)—C(5)	1.516 (10)
C(24)	0.1741 (3)	0.2636 (3)	0.8949 (3)	0.068 (3)	C(1)—C(2)	1.550 (7)	C(4A)—C(5A)	1.513 (10)
C(25)	0.1645 (3)	0.1944 (3)	0.9142 (3)	0.065 (3)	C(1A)—C(2A)	1.563 (8)		
C(26)	0.0934 (3)	0.1690 (3)	0.8872 (3)	0.057 (2)	C(12)—C(11)—C(16)	116.5 (5)	C(2)—C(1)—C(7)	108.0 (4)
C(27)	0.0717 (3)	0.1600 (3)	0.8061 (3)	0.049 (2)	C(12A)—C(11A)—C(16A)	115.4 (5)	C(2A)—C(1A)—C(7A)	107.6 (4)
C(31)	0.0575 (3)	0.2096 (3)	0.6828 (3)	0.046 (2)	C(2)—C(1)—C(1A)—C(2A)			49.5 (5)
C(32)	0.0642 (3)	0.2626 (3)	0.6411 (3)	0.052 (2)	C(7)—C(1)—C(1A)—C(2A)			169.4 (4)
C(33)	0.0752 (3)	0.2554 (3)	0.5732 (3)	0.060 (3)	C(7)—C(1)—C(1A)—C(7A)			-71.3 (5)
C(34)	0.0809 (3)	0.1957 (4)	0.5467 (3)	0.064 (3)	C(7)—C(1)—C(1A)—C(11A)			49.4 (5)
C(35)	0.0778 (3)	0.1428 (3)	0.5867 (3)	0.063 (3)	C(11)—C(1)—C(1A)—C(2A)			-71.8 (5)
C(36)	0.0663 (3)	0.1493 (3)	0.6549 (3)	0.055 (2)	C(11)—C(1)—C(1A)—C(11A)			168.2 (4)

(3) Molecule (III)

C(41)	0.0357 (3)	0.0870 (3)	0.2397 (3)	0.044 (2)	C(21)—C(21A)	1.627 (11)	C(21)—C(27)	1.556 (8)
C(42)	0.0463 (3)	0.1502 (3)	0.2019 (3)	0.050 (2)	C(21)—C(31)	1.565 (8)	C(24)—C(25)	1.513 (10)
C(43)	0.1082 (3)	0.1527 (3)	0.1728 (3)	0.059 (2)	C(21)—C(22)	1.536 (8)		
C(44)	0.0946 (4)	0.1337 (3)	0.0933 (3)	0.075 (3)	C(32)—C(31)—C(36)	116.7 (5)	C(22)—C(21)—C(27)	108.1 (4)
C(45)	0.0760 (3)	0.0638 (3)	0.0766 (3)	0.071 (3)	C(22)—C(21)—C(21A)—C(22A)			48.4 (5)
C(46)	0.0207 (3)	0.0391 (3)	0.1077 (3)	0.061 (2)	C(27)—C(21)—C(21A)—C(22A)			168.9 (4)
C(47)	0.0410 (3)	0.0298 (3)	0.1891 (3)	0.053 (2)	C(27)—C(21)—C(21A)—C(27A)			-70.6 (5)
C(51)	0.0911 (3)	0.0799 (3)	0.3096 (3)	0.047 (2)	C(27)—C(21)—C(21A)—C(31A)			48.9 (5)
C(52)	0.1201 (3)	0.1324 (3)	0.3508 (3)	0.053 (2)	C(31)—C(21)—C(21A)—C(22A)			-71.6 (5)
C(53)	0.1665 (3)	0.1245 (3)	0.4157 (3)	0.058 (2)	C(31)—C(21)—C(21A)—C(31A)			168.4 (4)
C(54)	0.1857 (3)	0.0655 (3)	0.4425 (3)	0.061 (3)				
C(55)	0.1600 (3)	0.0120 (3)	0.4020 (3)	0.063 (2)				
C(56)	0.1141 (3)	0.0195 (3)	0.3370 (3)	0.055 (2)				

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°)

(1)							
C(1)—C(2)	1.550 (5)	C(1)—C(5)	1.538 (5)				
C(1)—C(11)	1.538 (5)	C(1)—C(1A)	1.575 (7)				
C(2)—C(3)	1.525 (6)	C(3)—C(4)	1.526 (6)				
C(4)—C(5)	1.529 (6)	C(11)—C(12)	1.387 (6)				
C(11)—C(16)	1.387 (6)	C(12)—C(13)	1.375 (7)				
C(13)—C(14)	1.354 (6)	C(14)—C(15)	1.363 (9)				
C(15)—C(16)	1.380 (7)						
C(2)—C(1)—C(5)	98.9 (3)	C(2)—C(1)—C(11)	109.7 (3)				
C(5)—C(1)—C(11)	111.7 (3)	C(2)—C(1)—C(1A)	114.1 (2)				
C(5)—C(1)—C(1A)	113.1 (4)	C(11)—C(1)—C(1A)	109.1 (2)				
C(1)—C(2)—C(3)	105.4 (3)	C(2)—C(3)—C(4)	105.9 (3)				
C(3)—C(4)—C(5)	105.2 (3)	C(1)—C(5)—C(4)	105.0 (3)				
C(1)—C(11)—C(12)	121.6 (3)	C(1)—C(11)—C(16)	121.8 (4)				
C(12)—C(11)—C(16)	116.4 (4)	C(11)—C(12)—C(13)	121.2 (4)				
C(12)—C(13)—C(14)	121.7 (5)	C(13)—C(14)—C(15)	118.2 (5)				
C(14)—C(15)—C(16)	121.2 (5)	C(11)—C(16)—C(15)	121.3 (4)				
C(11)—C(1)—C(1A)—C(11A)		51.7 (4)					
C(2)—C(1)—C(1A)—C(2A)		-62.3 (4)					
C(2)—C(1)—C(1A)—C(5A)		49.7 (4)					
C(2)—C(1)—C(1A)—C(11A)		174.7 (4)					
Carbocyclic ring	R = Nitro	R = Cyano	R = Phenyl				
n							
3	1.476 (3) ^a						
4	1.508 (9)						
5	1.486 (4) ^b	1.537 (5) ^c	1.575 (5) ^d				
6	1.579 (3)	1.582 (10)	1.627 (5)				
7	1.601 (9)	1.591 (6)	1.630 (5)				
8			1.622 ^e				

Table 3. Central inter-ring C—C bond lengths (Å) and carbocyclic ring angles C(2)—C(1)—C(n) (°) at the central C(1) atom in various 1,1'-(R)(R)-1,1'-bicycloalkyl molecules

Carbocyclic ring	R = Nitro	R = Cyano	R = Phenyl
n			
3	1.476 (3) ^a		
4	1.508 (9)		
5	1.486 (4) ^b	1.537 (5) ^c	1.575 (5) ^d
6	1.579 (3)	1.582 (10)	1.627 (5)
7	1.601 (9)	1.591 (6)	1.630 (5)
8			1.622 ^e

5	105.4 ^b	101.9 ^c	98.9 ^d
6	110.2	108.9	105.5
7	113.2	111.4	108.0

References: (a) Kai, Knochel, Kwiatkowski, Dunitz, Oth, Seebach & Kalinowski (1982); (b) Lam, Huang & Hambley (1990); (c) Koh, Huang & Sim (1992); (d) this work; (e) Bernlöhner, Beckhaus, Lindner & Rüchardt (1984).

The three diphenyl bicycloalkyl compounds were synthesized by free radical dimerization using di-*tert*-butyl peroxide as initiator (Huang & Lim, 1967). The starting material, phenyl cycloalkane, was mixed with di-*tert*-butyl peroxide in the molar ratio 2:1 and heated for about 30 h at ~403 K under N₂. After cooling, both the volatile by-products and the starting materials were removed by distillation under reduced pressure. The residue was then purified chromatographically using silica gel (60–200 mesh, E. Merck). Over a period of several months, single crystals of (1) were grown in a mixture of water/*n*-hexane/acetonitrile; (2) and (3) were crystallized from ethanol and *n*-hexane, respectively, after chromatographic purification. All starting materials were commercially available except phenyl cycloheptane which was prepared by the method of Corson & Ipatieff (1943). The m.p.'s for (1), (2) and (3) were 410.5, 455 and 412 K, respectively [literature values 414–415, 455–457 and 415.5–416 K (Beckhaus, Schoch & Rüchardt, 1976)].

All three structures were solved by direct methods using XS (*SHELXTL-Plus*; Siemens, 1989) and refined by full-matrix least-squares analysis using XLS (Sheldrick, 1976, 1985). The data were reduced and Lorentz and polarization corrections applied using the programs mentioned. C atoms were refined anisotropically in all three structures whereas H atoms were placed at calculated positions with fixed isotropic thermal parameters.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55798 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1030]

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Structure of *N*-(2,6-Dimethylphenyl)-5-methylisoxazole-3-carboxamide and Molecular-Orbital Study of C—H···O Bonded Dimers

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Abstract

The molecular structure of the title compound comprises two nearly orthogonal planar systems. The main feature of the crystalline structure is the existence of C—H···O interactions linking two molecules about the centers of inversion. From crystallographic data, charges and interaction enthalpy are calculated for the monomer and the dimer by means of the AM1 (Austin model 1) semi-empirical method. A substantial stabilization of the molecular structure through dimer formation is observed.