1—2—16—15—10—9, and the 8·0 (3)° torsion angle S(29)—C(1)—C(2)—C(3) shows relatively little departure from an ideal boat in the chair–boat conformation of the thiabicyclononane moiety.

The difference in geometry about the C(1)—C(2) bond affects the positioning of the rigid benzo group relative to O(32) of the sulfone. In adduct *D* the benzo group is tilted toward the sulfone, producing an intramolecular contact of 2·869 (4) Å between O(32) and C(10), appreciably less than the van der Waals radius sum of 3·10 Å (Pauling, 1960). In adduct *B* this nonbonded contact is 3·218 (4) Å.

McCabe & Sim (1981, 1982) have studied the geometry of the 9-thiabicyclo[3.3.1]nonane 9,9-dioxide system in the 2,6-dichloro and 2,6-dinitrato derivatives. Despite the resulting close contact between C(3) and C(7), and their hydrogens, both compounds assume chair–chair conformations, as does the 9-thiabicyclo[3.3.1]nonane moiety in adduct *B*. In adduct *B* we find C(3)···C(7) = 3·077 (5) and H(3*B*)···H(7*B*) = 1·88 (6) Å. These distances are even shorter than the values 3·120 (4) and 3·128 (2) Å found for C(3)···C(7) in the 2,6-dichloro and 2,6-dinitrato derivatives, and 2·071 (28) Å for the corresponding H···H distance in 2,6-dinitrato derivative. As McCabe & Sim (1982) point out, these X-ray values for the H···H distance may understate the closeness of approach, as the true internuclear C—H distances tend to be longer than the X-ray values.

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Electron Density Distribution in a Bicyclo[1.1.0]butane

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Abstract

The difference electron densities in the bicyclo-[1.1.0]butane derivative 4-phenyl-2,4,6-triazapentacyclo[5.4.2.$0^{2,6}$.$0^{8,10}$.$0^{9,11}$]tridec-12-en-3,5-dione (I) have been determined experimentally at 98 (1) K from X-ray (Mo $K\alpha$, λ = 0·71069 Å) diffraction data measured to $(\sin\theta/\lambda)_{max}$ = 1·15 $Å^{-1}$. Crystal data: $C_{16}H_{13}N_3O_2$, M_r = 279·3, orthorhombic, *Pbca*, a = 11·340 (1), b = 15·037 (1), c = 15·405 (1) Å, V = 2626·9 (6) $Å^3$, Z = 8, D_x = 1·38 Mg m^{-3}, μ = 0·0901 mm^{-1}, $F(000)$ = 1168, final R = 0·052 for 3605 reflections. Based on the degree of inversion from tetrahedral geometry of the bridgehead C atoms in polycyclic systems, compound (I) lies on the transition from open bicyclo[1.1.0]butanes to propellanes. The very weak difference density contribution in the central C(1)—C(3) bond fits into the graduation along this line. The bonding maxima in the bicyclo[1.1.0]butane moiety and, to a lesser

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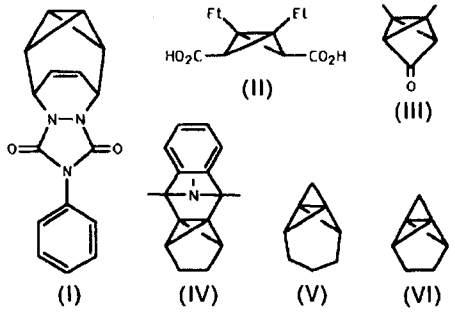
extent in some bonds of the triazolinedione ring, are shifted outwards from the internuclear axes. The bonds are bent.

Introduction

The structure determination of (I) at room temperature has been discussed previously (Christl, Lang, Reimann & Irngartinger, 1984). Experimentally determined difference electron densities ($X-X$) show significant maxima in the bridging bonds of the bicyclo[1.1.0]butane systems (II) (Eisenstein & Hirshfeld, 1983) and (III) (Irngartinger & Goldmann, 1982), but the maxima are shifted from the internuclear connecting lines, demonstrating that the bonds are bent. In the corresponding group of molecule (IV), however, which is incorporated in a [3.1.1]propellane system, the density maximum on the central bond was missing (Chakrabarti, Seiler, Dunitz, Schlüter & Szeimies, 1981). In the recently reported [1.1.1]propellanes (V) and (VI) (Seiler, Belzner, Bunz & Szeimies, 1988) the difference density is negative. Obviously, the inverted tetrahedral geometries of the bridgehead atoms have an effect on the difference density of the bridging bond. According to the inversion parameters (Table 1), compound (I) is intermediate between (IV) and (II). Therefore we determined the difference electron density in the bridging bond of (I), a compound which has bridgehead C atoms with a relatively high degree of inversion, but which is not a propellane system.

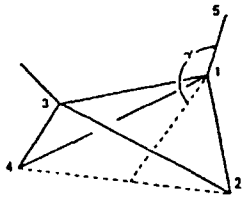


Experimental

Crystal grown from ethanol, crystal dimensions 0·35 × 0·3 × 0·2 mm. Intensities were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator and a liquid N_2 gasflow set-up. Cell parameters were determined from 40 reflections ($20 < \theta < 28°$). Two unique sets of reflections up to $\theta = 28°$ were measured with the ω–2θ scan technique. After structure refinement the reflections with $|F_{calc}| > 3\cdot0$ were calculated between $\theta = 28$ and 55°, and were measured twice. The total number of reflections was 13 806. An absorption correction was applied. Transmission factors were in the range 0·95–0·99; range of indices 26, 34 and 35 for h, k and l, respectively. The intensities were averaged: $R_{int} = 0\cdot03$. The discrepancy function minimized in the full-matrix least-squares refinement was $wR(F^2) = \sum w(k^2F_o^2 - F_c^2)^2/\sum wk^4F_o^4$, in which $w = 1/\sigma^2(F_o^2)$ (C, N, O anisotropic, H isotropic; no extinction correction). Low-order refinement with the data up to $\sin\theta/\lambda = 0\cdot75$ Å^{-1}: 3053 reflections

Table 1. *Inversion parameters, difference densities and distances of the central bond in bicyclo*[1.1.0]*butane groups*

The inversion parameter is the angle between the bonding vector C(1)—C(5) or C(1)—H(5) and the plane through the atoms C(1), C(2), C(4). The electron density of compound (II) (Eisenstein & Hirshfeld, 1983) is obtained from a static model. Therefore the comparison with the $X-X$ densities of the other compounds is restricted.



Molecule	ν (°)	Max. C(1)—C(3) (e Å^{-3})	$d_{1,3}$ (Å)
(VI)	78·8	Negative	1·577 (1)
(V)	81·8	Negative	1·582 (1)
(IV)	144·1	0·05	1·574 (1)
(I)	167·2	0·12	1·512 (5)
(II)	183·6	0·40	1·452 (2)
(III)	197·5	0·28	1·417 (1)

Table 2. *Atomic fractional coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å$^2 \times 10^3$)

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

	x	y	z	U_{eq}
C(1)	7770 (3)	1832 (2)	4600 (3)	212 (12)
C(2)	8735 (3)	1183 (2)	4367 (2)	190 (10)
C(3)	7977 (3)	1015 (2)	5150 (4)	232 (13)
C(4)	8045 (3)	1916 (2)	5551 (3)	185 (10)
C(5)	9230 (3)	2321 (2)	5839 (2)	153 (8)
C(6)	10149 (3)	1616 (2)	6019 (2)	170 (9)
C(7)	10561 (3)	1188 (2)	5320 (2)	176 (10)
C(8)	10041 (3)	1464 (2)	4461 (2)	160 (9)
N(9)	10147 (2)	2442 (1)	4413 (2)	151 (7)
C(10)	9812 (3)	2894 (2)	3680 (2)	181 (10)
N(11)	9274 (3)	3677 (2)	3970 (2)	164 (8)
C(12)	9097 (2)	3632 (2)	4861 (2)	138 (8)
N(13)	9705 (2)	2902 (1)	5152 (2)	131 (7)
O(14)	8538 (3)	4157 (2)	5307 (2)	196 (9)
O(15)	9978 (6)	2674 (2)	2933 (2)	321 (15)
C(16)	8761 (3)	4312 (2)	3401 (2)	154 (9)
C(17)	7835 (3)	4051 (2)	2861 (3)	199 (11)
C(18)	7345 (3)	4665 (3)	2290 (3)	226 (13)
C(19)	7775 (4)	5534 (3)	2265 (3)	237 (13)
C(20)	8688 (4)	5790 (2)	2818 (2)	223 (12)
C(21)	9197 (3)	5179 (2)	3383 (2)	180 (9)

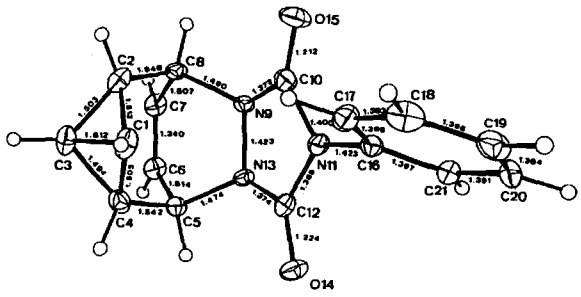


Fig. 1. Bond lengths (Å) of (I). The standard deviations are 0·003–0·006 Å.

{including 525 unobserved reflections [$I < 2{\cdot}24\sigma(I)$]}, 242 variables, observations per variable: 12·6, $R(F) = 0{\cdot}04$, $wR(F^2) = 0{\cdot}005$, $S = 1{\cdot}83$, $(\Delta/\sigma) < 0{\cdot}1$. The coordinates and anisotropic displacement parameters of the non-H atoms were further refined with the high-order data $0{\cdot}75 < \sin\theta/\lambda < 1{\cdot}15$ Å^{-1}: 1899 reflections (including 822 unobserved reflections), 190 variables, observations per variable: 10, $R(F) = 0{\cdot}068$, $wR(F^2) = 0{\cdot}024$, $S = 0{\cdot}98$, $(\Delta/\sigma) < 0{\cdot}1$. The difference density distributions were calculated with the data up to $\sin\theta/\lambda = 0{\cdot}75$ Å^{-1}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final parameters are given in Table

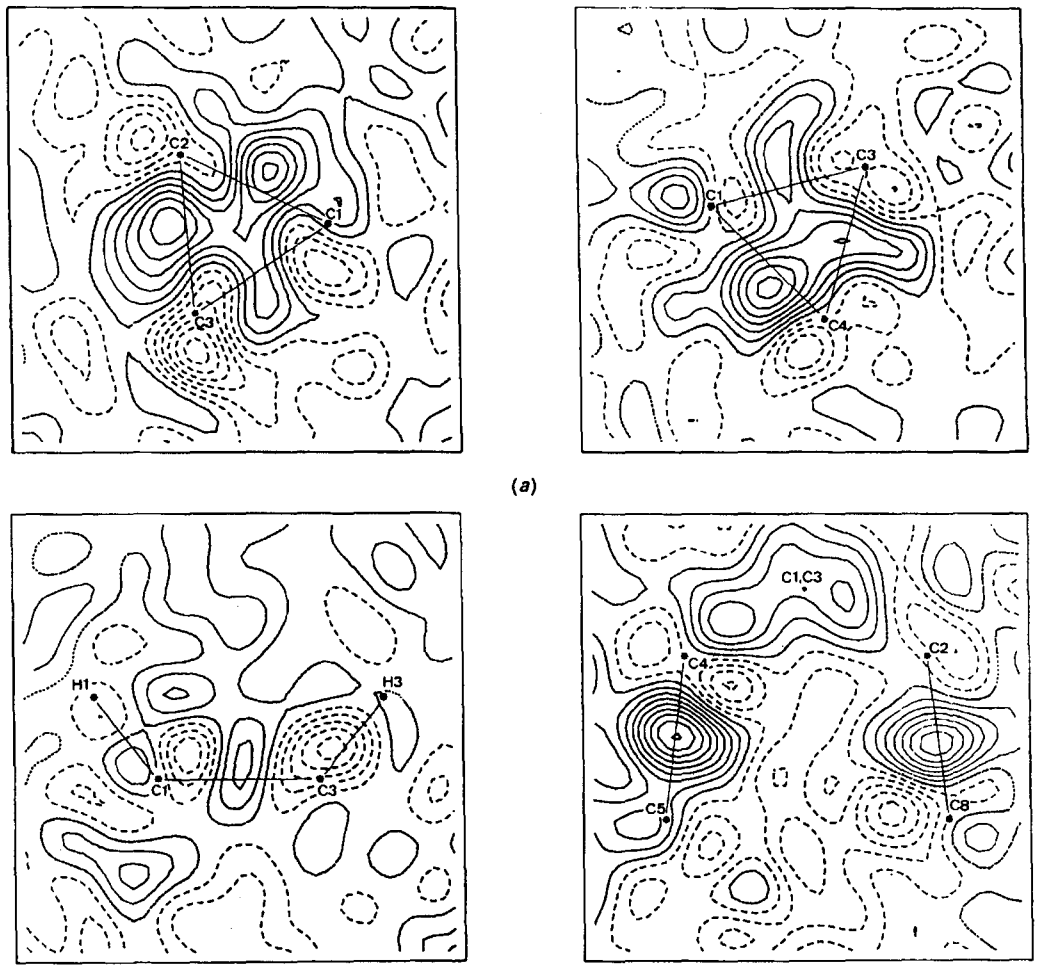


Fig. 2. Difference density ($X - X$) of (I). The contour intervals are 0·05 e Å^{-3}. The zero line is dotted, negative regions have dashed lines. (*a*) Sections in the plane of the three-membered rings C(1), C(2), C(3) and C(1), C(3), C(4). (*b*) Plane bisecting the interplanar angle between the three-membered rings through the central bond C(1)—C(3), and the section perpendicular to this bond through its midpoint.

2.* Computer programs used: *SDP* (Frenz, 1982) and local programs.

Discussion

The numbering of the atoms and the bond distances are shown in Fig. 1. The difference densities were calculated in several sections and are shown in Fig. 2. Except near atomic positions the standard deviation for the difference density is $\sigma(\Delta\rho) = 0{\cdot}06$ e Å^{-3} calculated according to the procedure of Rees (1976). The density maxima in the bonds of the three-membered rings (Fig. 2*a*) are shifted from the internuclear axes, demonstrating that the bonds are bent. The density in the central bond C(1)—C(3) (Figs. 2*a* and 2*b*) is the lowest of all the bonding maxima of the bicyclo[1.1.0]butane moiety. Its height is intermediate between the bicyclo[1.1.0]butanes and the propellanes (Table 1). The intermediate position of (I) is also indicated by the structural parameters (Table 1). The density maxima on the bonds of the phenyl ring appear clearly (Fig. 2*c*).

* Lists of H-atom positions, anisotropic displacement parameters, bond lengths, bond angles and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52243 (68 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

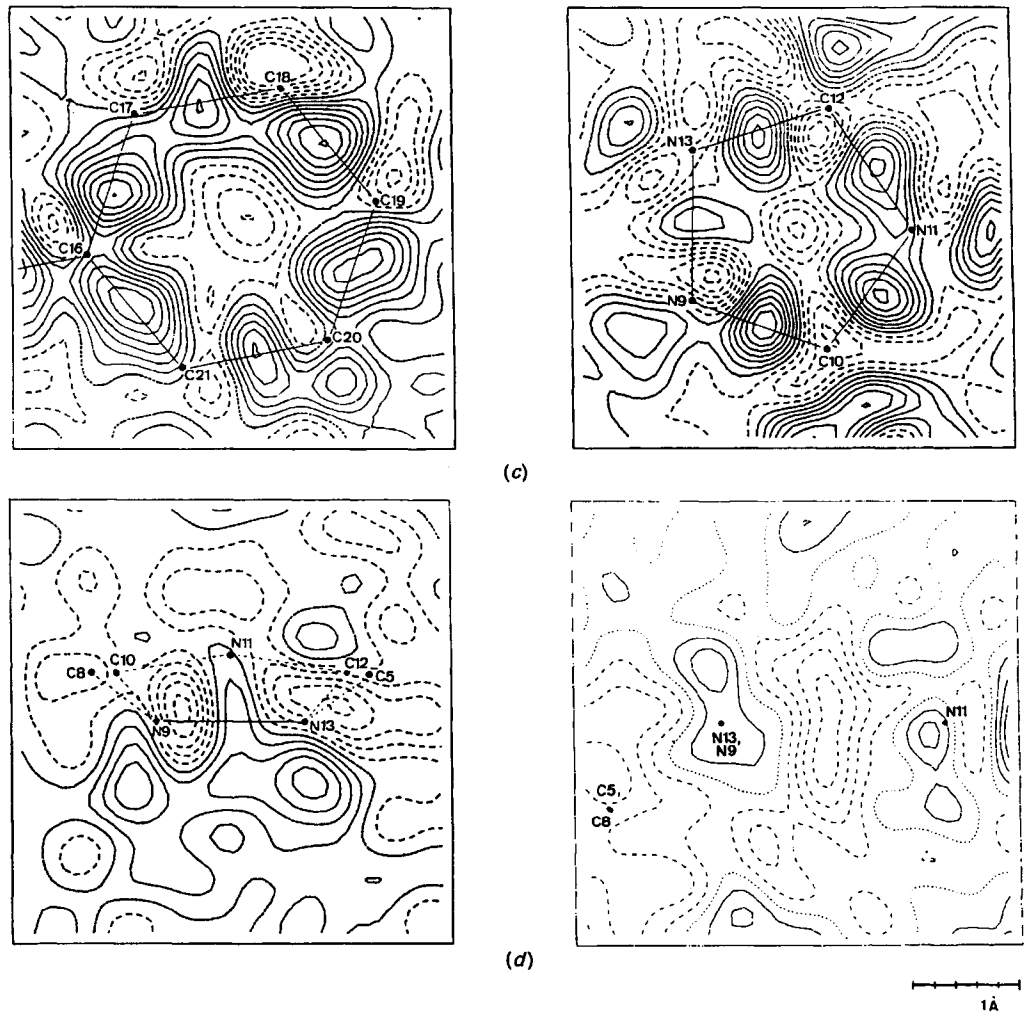


Fig. 2 (*cont.*) (*c*) Section in the plane of the phenyl ring and the triazolinedione ring. (*d*) Plane bisecting the dihedral angle between the planes through the atoms C(5), N(13), N(9), C(8) and the triazolinedione ring; plane bisecting the bond angle C(10)—N(11)—C(12) and perpendicular to the plane of these atoms.

The bond angles C(10)—N(11)—C(12) 109·8 (2)°, N(9)—C(10)—N(11) 106·0 (2)° and N(11)—C(12)—N(13) 106·7 (2)° deviate considerably from the standard angle of 120° for sp^2 hybridized atoms. The N(9) and N(13) atoms, however, are sp^3 hybridized and have smaller standard bond angles. The pyramidal geometry is described by the deviation of these N atoms by 0·34 Å from the plane of the substituted atoms as against only 0·096 Å for N(11), which is partially sp^2 hybridized. Therefore, the angular strain is particularly high in the C(10)—N(11) and C(12)—N(11) bonds. Accordingly, the difference density maxima of C(10)—N(11) and C(12)—N(11) in the triazolinedione ring are shifted outwards by small amounts from the bond axes (Fig. 2*c*) indicating bent bonds in this part of the five-membered ring.

The lone pair of N(11) participates in conjugation to both carbonyl groups. Therefore hardly any density can be recognized on the top of the flattened pyramid of N(11) Fig. 2*d*). In a suitable section through the N(9) and N(13) atoms (Fig. 2*d*) difference density maxima are observed at the positions of the lone pairs. The electron density in the N(9)—N(13) bond (Fig. 2*c*) is low. The low difference densities on bonds between heteroatoms have already been discussed in the literature (Irngartinger, Kallfass, Prinzbach & Klingler, 1989).

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Structure and Conformations of Two Cycloisomeric Hexapeptides: *cyclo*(L-Leu-L-Phe-Gly-D-Phe-L-Leu-Gly-) Trihydrate and *cyclo*(L-Phe-L-Leu-Gly-D-Leu-L-Phe-Gly-) Trihydrate

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Abstract

cyclo(L-Leucyl-L-phenylalanyl-glycyl-D-phenylalanyl-L-leucyl-glycyl-) trihydrate (IV), $C_{34}H_{46}N_6O_6.3H_2O$, $M_r = 688{\cdot}8$, monoclinic, $P2_1$, $a = 11{\cdot}720$ (2), $b = 36{\cdot}354$ (4), $c = 8{\cdot}888$ (1) Å, $\beta = 103{\cdot}88$ (1)°, $V = 3676{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}244$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 7{\cdot}6$ cm^{-1}, $F(000) = 1480$, $T = 138$ K, final $R = 0{\cdot}052$ for 7661 unique reflections. *cyclo*(L-Phenylalanyl-L-leucyl-glycyl-D-leucyl-L-phenylalanyl-glycyl-) trihydrate (V), $C_{34}H_{46}N_6O_6.3H_2O$, $M_r = 688{\cdot}8$, triclinic, $P1$, $a = 11{\cdot}668$ (3), $b = 19{\cdot}111$ (5), $c = 8{\cdot}527$ (1) Å, $\alpha = 101{\cdot}54$ (2), $\beta = 93{\cdot}42$ (2), $\gamma = 94{\cdot}27$ (2)°, $V = 1852{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}235$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 7{\cdot}5$ cm^{-1}, $F(000) = 740$, $T = 138$ K, final $R = 0{\cdot}063$ for 7574 unique reflections. Peptides IV and V both have two independent conformers (molecules *A* and *B*). The peptide ring in each case contains one β(I) turn and one β(II′) turn. *A* molecules in both structures have two transannular N—H···O hydrogen bonds, while *B* molecules form only one strong transannular hydrogen bond. The conformational differences between the two independent molecules (*A* and *B*) are much larger than the differences between the corresponding molecules of the two structures (*A* and *A*, and *B* and *B*). The crystal structures of the two peptides are very similar and consist of parallel bands of hydrophobic side chains and polar peptide regions. In each structure, molecules are stacked one over another with the hexapeptide ring lying perpendicular to the axis of the stack. The water molecules form well

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