

Table 2. *Hydrogen-bond distances (Å) with standard deviations in parentheses*

O(1)···O	2.60 (1)	H(O1)···O	1.88 (5)
O(2)···N ⁱ	3.02 (1)	O(2)···H(N ^A)	2.25 (4)
O(2)···N ⁱⁱ	3.04 (4)	O(2)···H(N ^B)	2.28 (5)

Symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

amino groups and carbonyl groups of PABA are hydrogen bonded head-to-tail. Hydrogen-bond distances are listed in Table 2. These show normal values (Pauling, 1960; Sutton, 1958). Other intermolecular distances are quite normal. The shortest intermolecular distance is 3.411 (9) Å for C(1)···N(2)($2 - x, \frac{1}{2} + y, \frac{1}{2} - z$), which is not a hydrogen bond. The interaction mode and the reason why PABA and DMI form a one-to-one complex can be well understood. These results should be useful for understanding the properties of DMI-drug complexes. The least-squares plane of C(2), C(3), C(4), C(5), C(6) and C(7) was calculated. The deviations of the other non-hydrogen atoms of PABA from the plane are 0.034 (8) to 0.087 (9) Å. For DMI, high planarity is also observed. The deviations of CD and CE from the least-squares plane of CA, N(1),

CB, CC and N(2) are 0.180 (11) and 0.165 (11) Å, respectively (Ito, 1982). The sum of the three bond angles around N(1) is 357.2 (18)° and that around N(2) is 356.5 (18)°. Thus, the arrangements of bonds around N(1) and N(2) are quasi-planar.

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(6R*,7S*,10R*,11S*)-6,6a,7,8,9,10,10a,11-Octahydro-6,11-dimethyl-12-phenyl-6,11-imino-7,10-methano-5H-dibenzo[*b,e*]azepine

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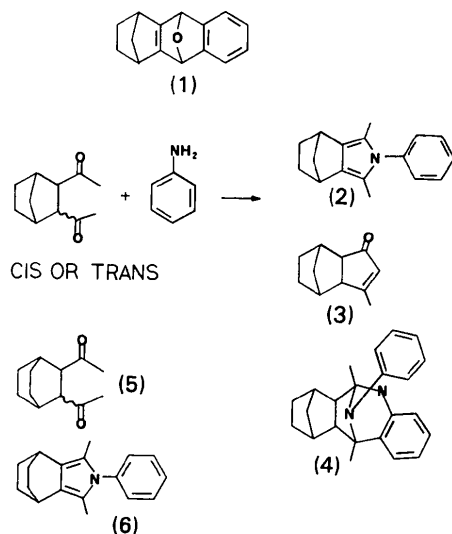
Abstract. C₂₃H₂₆N₂, *M_r* = 330.48, triclinic, *P* $\bar{1}$, *a* = 11.276 (4), *b* = 11.510 (4), *c* = 8.369 (4) Å, α = 113.40 (3), β = 99.14 (3), γ = 108.94 (3)°, *V* = 889.6 (6) Å³, *Z* = 2, *D_m* = 1.230, *D_x* = 1.234 g cm⁻³, $\lambda(\text{Cu K}\alpha)$ = 1.54178 Å, μ = 5.57 cm⁻¹, *F*(000) = 356, room temperature (295 K), *R* = 0.040 for 2099 independent observed reflections. The molecule can be described as composed of a seven-membered ring fused to a six-membered saturated ring and a phenyl ring. The six-membered ring is bridged by a methylene group while the seven-membered ring is bridged by an *N*-phenyl nitrogen. The seven-membered ring can be described in terms of a planar moiety folded along an axis through the bridged atoms forming a dihedral angle of 108.4 (3)°. There are a number of intramolecular

H···H contacts less than 2.50 Å, and molecular-mechanics calculations are used to analyze these interactions.

Introduction. The pyramidalization of the C(*sp*²) carbon atoms in *syn*-sesquinorbornenes is well documented (Watson, 1983), and compound (1) with a 22.1 (2)° fold along the C=C bond represents the largest such deviation reported (Watson, Galloy, Grossie, Bartlett & Combs, 1984). It is of interest to prepare the nitrogen analogue of this compound, and synthetic routes involving pyrroles have been investigated. 1,4-Diketones are known to undergo condensation with aniline, in the presence of acids, to give the corresponding *N*-phenyl pyrroles (Wynberg & Klunder, 1969). When 2,3-diacetylnorbornane was treated with aniline in refluxing ethanol for 3.0 d,

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pyrrole (2) (25%) and compounds (3) (20%) and (4) (10%) were obtained. Although (4) can be regarded as a secondary product arising from the reaction of (2) with aniline, refluxing (2) with aniline in the presence of HCl gave no reaction. To the best of our knowledge the formation of compounds similar to (4) from a reaction between 1,4-diones and aniline is unprecedented (Sutherland, 1979). Interestingly, the bicyclo[2.2.2] system with aniline gives (6) as the only product. The mechanism for the formation of (4) is under investigation.



Experimental. To a mixture of 1.0 g of 2,3-diacetylnorbornane and 1.0 g of freshly distilled aniline in 25 ml absolute EtOH was added 8 drops of conc. HCl, and the solution refluxed for 3 d. After cooling the EtOH was stripped off under vacuum and the dark residue taken up in 30 ml of Et₂O. The ether solution was washed with 10% HCl, water and brine, and dried over MgSO₄. The ether was evaporated off and the residue subjected to distillation at 338 K/0.05 mm Hg. A mixture of the starting diketone and (3) was obtained as the distillate. The residue from the distillation was chromatographed over neutral alumina, with hexane:Et₂O (2:1) as eluant. First to elute was (2) (330 mg) followed by (4) (180 mg). For (4): m.p. 441–442 K; ¹H NMR (CDCl₃): δ 6.95–7.20 (*m*,5H), 6.88 (*m*,2H), 6.70 (*t*,1H), 6.45 (*d*,1H), 4.08 (*brs*,1H), 2.59 (*m*,1H), 2.20–2.33 (*m*,2H), 2.06 (*m*,1H), 1.45 (*m*,1H), 1.40 (*s*,3H), 1.28 (*s*,1H), 1.20 (*s*,3H), 1.00–1.10 (*m*,2H), 0.80–1.00 (*m*,2H). ¹³C NMR: 143.6 (*s*), 143.0 (*s*), 132.4 (*s*), 129.4 (2C,*d*), 128.1 (2C,*d*), 127.1 (*d*), 124.8 (*d*), 123.1 (*d*), 118.0 (*d*), 114.2 (*d*), 76.5 (*s*), 65.2 (*s*), 61.9 (*d*), 61.4 (*d*), 38.7 (*d*), 38.4 (*d*), 33.9 (*t*), 29.6 (*t*), 29.1 (*t*), 21.2 (*q*), 17.9 (*q*). IR (KBr): 3350 (*brs*), 2800, 2750, 1600, 1460, 1260, 1120, 1040, 740, 700 cm⁻¹. Calc. for C₂₃H₂₆N₂: C, 83.64; H, 7.88; N, 8.48%. Found: C, 83.58; H, 7.99; N, 8.60%.

White prismatic-shaped crystal recrystallized from absolute EtOH, 0.45 × 0.50 × 0.21 mm; Syntex P2₁ diffractometer; $\theta:2\theta$ scan, variable scan rate; all accessible independent reflections collected within range $8 \leq 2\theta \leq 120^\circ$; graphite-monochromated radiation; lattice parameters from least-squares refinement of 15 reflections ($9.0 \leq 2\theta \leq 25.0^\circ$) with angles measured by centering routine associated with diffractometer system; no systematic absences; space group P1 or P $\bar{1}$ with P $\bar{1}$ consistent with statistics; 1 monitored reflection (03 $\bar{1}$) showed no change in intensity greater than $2\sigma(I)$; 2425 independent reflections measured ($0 \leq h \leq 12$, $-12 \leq k \leq 11$, $-9 \leq l \leq 8$), 2099 intensities greater than $3\sigma(I)$; 51 sets of equivalent reflections averaged ($R_{\text{int}} = 0.011$); Lorentz and polarization corrections applied, no absorption correction; direct methods (MULTAN78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all 25 nonhydrogen atoms; least-squares refinement followed by difference Fourier synthesis led to location of all H atoms; H-atom parameters refined isotropically but held fixed during final cycles of anisotropic refinement and bond lengths finally fixed at 1.08 Å by scaling (for better evaluation of intramolecular contacts and comparison with molecular-mechanics calculations); full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$ [derived from counting statistics evaluated by Syntex (1976) routine]; 226 parameters refined, final $R = 0.040$, $wR = 0.054$, $S = 2.81$, $(\Delta/\sigma)_{\text{max}} = 0.13$ (coordinate), $(\Delta/\sigma)_{\text{av}} = 0.044$, highest peak in final difference Fourier map $|0.12| \text{ e } \text{\AA}^{-3}$; locally written programs for data reduction, ORTEPII (Johnson, 1971), MULTAN78 for direct-methods calculations and XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all others; atomic scattering factors for C and N from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Table 1 lists atomic positional parameters and U_{eq} values while Table 2 lists interatomic distances and valence angles.*

Modified molecular-mechanics programs MMPI (Allinger, 1975) and MM2 (Allinger & Yuh, 1980) were used to calculate the lowest-energy conformation of the title compound. Parameters derived previously for norbornane and sesquinorbornane systems were used for the six-membered ring and the bridging methylene group. Parameters involving the trigonal and pyramidal nitrogen atoms were derived by trial and error from other structural data while torsion-angle constants were estimated.

* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, molecular-mechanics calculated distances and angles and unique molecular-mechanics parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42631 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) for nonhydrogen atoms and equivalent isotropic thermal parameters U_{eq} ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^\dagger
C(1)	3499 (2)	8304 (2)	-1194 (2)	50 (1)
C(2)	4023 (2)	7392 (2)	-2054 (3)	58 (1)
C(3)	3843 (2)	6261 (2)	-1764 (2)	55 (1)
C(4)	3169 (2)	6045 (2)	-598 (2)	49 (1)
C(4a)	2659 (2)	6976 (2)	306 (2)	42 (1)
N(5)	1975 (2)	6772 (2)	1480 (2)	49 (1)
C(6)	1487 (2)	7782 (2)	2464 (2)	41 (1)
C(6a)	2668 (2)	9162 (2)	3992 (2)	42 (1)
C(7)	2371 (2)	10161 (2)	5574 (2)	53 (1)
C(8)	3719 (2)	11338 (2)	6992 (3)	61 (1)
C(9)	4200 (2)	12210 (2)	6026 (3)	59 (1)
C(10)	3075 (2)	11420 (2)	4167 (2)	50 (1)
C(10a)	3148 (2)	10040 (2)	3010 (2)	40 (1)
C(11)	2204 (2)	9086 (2)	975 (2)	40 (1)
C(11a)	2809 (2)	8118 (2)	-18 (2)	40 (1)
N(12)	991 (1)	8266 (1)	1226 (2)	38 (1)
C(13)	1864 (2)	10946 (2)	4743 (3)	59 (1)
C(14)	-208 (2)	7325 (2)	-310 (2)	41 (1)
C(15)	-271 (2)	6546 (2)	-2113 (2)	56 (1)
C(16)	-1485 (2)	5714 (2)	-3526 (3)	64 (1)
C(17)	-2648 (2)	5625 (2)	-3168 (3)	59 (1)
C(18)	-2601 (2)	6385 (2)	-1396 (3)	57 (1)
C(19)	-1397 (2)	7236 (2)	13 (2)	49 (1)
C(20)	465 (2)	7086 (2)	3162 (2)	51 (1)
C(21)	1902 (2)	9888 (2)	26 (3)	53 (1)

$$\dagger U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\alpha + 2U_{13}aca^*c^*\cos\alpha + 2U_{23}bcb^*c^*\cos\beta].$$

Discussion. Fig. 1 is an ORTEPII (Johnson, 1971) drawing of the title compound. The molecular-mechanics calculated distances differ from the observed values by an average of 0.005 Å for the norbornane part of the molecule and by 0.01 Å for the remainder. The valence angles for the norbornane part differ by an average of 0.9°, the phenyl ring angles by 0.6° and the remainder of the molecule by 1.5°. The experimental C—H distances were scaled to a value of 1.08 Å to permit better comparisons with the calculated values. In the text the molecular-mechanics calculated values are given in parentheses following the experimentally derived values.

The phenyl ring is almost perpendicular to the remainder of the molecule with no conjugation to the nitrogen lone pair. N(12) exhibits a pyramidal geometry with the nitrogen lying 0.338 (3) (0.282) Å out of the plane of the three attached atoms. Molecular-mechanics calculations indicate that the pyramidalization arises from the compression of the C(6)N(12)C(11) angle to 104.3 (1)° and an attractive interaction between H(13b) and N(12), H(13b)⋯N(12) = 2.43 (2.47) Å. Even if N(sp²) hybridization is introduced and N(12) is included in the π system, the geometry becomes pyramidalized. N(5) is trigonally coordinated, and the lone pair is conjugated with the fused phenyl ring. The N(5)—C(4a) distance of 1.386 (3) (1.394) Å is consistent with delocalization. The phenyl ring, N(5), C(6) and C(11) are coplanar and make an angle of 108.0 (4) (103.6)° with the C(6)C(6a)C(10a)C(11) plane and

121.2 (3) (119.0)° with the C(6)N(12)C(11) plane. The interplanar angle between C(6)N(12)C(11) and C(6)C(6a)C(10a)C(11) is 130.8 (5) (137.3)°. This indicates a greater repulsion of the bridging atoms in the calculated gas-phase conformation.

Table 2. Interatomic distances (Å) and valence angles (°)

C(1)—C(2)	1.381 (3)	C(8)—C(9)	1.545 (4)
C(1)—C(11a)	1.386 (3)	C(9)—C(10)	1.535 (3)
C(2)—C(3)	1.375 (4)	C(10)—C(10a)	1.535 (3)
C(3)—C(4)	1.377 (3)	C(10)—C(13)	1.526 (3)
C(4)—C(4a)	1.394 (3)	C(10a)—C(11)	1.555 (2)
C(4a)—N(5)	1.386 (3)	C(11)—C(11a)	1.528 (3)
C(4a)—C(11a)	1.409 (3)	C(11)—N(12)	1.489 (2)
N(5)—C(6)	1.460 (3)	C(11)—C(21)	1.517 (4)
C(6)—C(6a)	1.551 (2)	N(12)—C(14)	1.430 (2)
C(6)—N(12)	1.474 (3)	C(14)—C(15)	1.391 (3)
C(6)—C(20)	1.515 (3)	C(14)—C(19)	1.389 (3)
C(6a)—C(7)	1.539 (3)	C(15)—C(16)	1.387 (3)
C(6a)—C(10a)	1.561 (3)	C(16)—C(17)	1.372 (3)
C(7)—C(8)	1.538 (2)	C(17)—C(18)	1.372 (2)
C(7)—C(13)	1.527 (4)	C(18)—C(19)	1.380 (2)
C(2)C(1)C(11a)	121.5 (2)	C(10)C(10a)C(11)	118.7 (2)
C(1)C(2)C(3)	119.5 (2)	C(6a)C(10a)C(11)	104.0 (1)
C(2)C(3)C(4)	120.7 (2)	C(6a)C(11a)C(10)	103.2 (1)
C(3)C(4)C(4a)	120.2 (2)	C(10a)C(11)C(11a)	107.1 (2)
C(4)C(4a)N(5)	121.0 (2)	C(10a)C(11)C(21)	113.8 (2)
C(4)C(4a)C(11a)	119.5 (2)	C(11a)C(11)C(21)	113.7 (2)
N(5)C(4a)C(11a)	119.5 (2)	C(10a)C(11)N(12)	100.9 (2)
C(4a)N(5)C(6)	120.3 (2)	C(11a)C(11)N(12)	109.6 (2)
N(5)C(6)C(6a)	110.0 (1)	N(12)C(11)C(21)	110.8 (2)
N(5)C(6)N(12)	108.7 (1)	C(1)C(11a)C(11)	124.1 (2)
N(5)C(6)C(20)	107.6 (2)	C(4a)C(11a)C(11)	117.3 (2)
C(6a)C(6)N(12)	100.9 (1)	C(1)C(11a)C(4a)	118.5 (2)
C(6a)C(6)C(20)	114.4 (1)	C(6)N(12)C(14)	119.4 (1)
N(12)C(6)C(20)	114.9 (2)	C(6)N(12)C(11)	104.3 (1)
C(6)C(6a)C(7)	117.9 (2)	C(11)N(12)C(14)	120.5 (2)
C(6)C(6a)C(10a)	105.1 (1)	C(7)C(13)C(10)	94.4 (2)
C(7)C(6a)C(10a)	102.3 (2)	N(12)C(14)C(15)	125.1 (2)
C(6a)C(7)C(8)	106.9 (2)	N(12)C(14)C(19)	117.2 (2)
C(6a)C(7)C(13)	103.5 (2)	C(15)C(14)C(19)	117.6 (1)
C(8)C(7)C(13)	100.8 (2)	C(14)C(15)C(16)	120.6 (2)
C(7)C(8)C(9)	103.3 (2)	C(15)C(16)C(17)	120.7 (2)
C(8)C(9)C(10)	102.9 (1)	C(16)C(17)C(18)	119.3 (2)
C(9)C(10)C(13)	101.0 (2)	C(17)C(18)C(19)	120.4 (2)
C(9)C(10)C(10a)	107.5 (2)	C(14)C(19)C(18)	121.3 (2)
C(10a)C(10)C(13)	102.9 (1)		

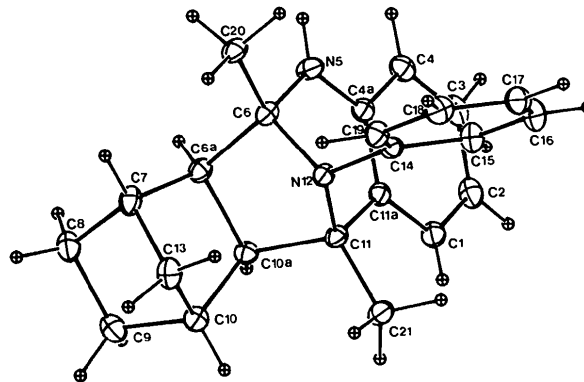


Fig. 1. ORTEP drawing of (4). Thermal ellipsoids are drawn at the 35% probability level.

A number of short intramolecular H...H contacts influence the conformation of the molecule. The H(6a)...H(8a) and H(10a)...H(9b) distances are 2.24 (2.47) and 2.34 (2.38) Å, respectively. The folding of the six-membered ring along the C(7)...C(10) axis gives an interplanar angle of 111.4 (3) (113.8)°. The short intramolecular contacts cannot be relieved by any significant expansion of this interplanar angle due to contacts H(13a)...H(8b) and H(13a)...H(9a) = 2.59 (2.64) and 2.57 (2.62) Å, respectively. The interplanar angles for C(10)C(13)C(7) with C(7)C(8)C(9)C(10) and C(6a)C(7)C(10)C(10a) are 122.5 (3) (121.8)° and 126.1 (3) (124.5)°. The 126.1 and 130.8° interior interplanar angles indicate a significant contact between H(13b) and the N(12) lone pair. Other close contacts are H(7)...H(20b) = 2.25 (2.45), H(1)...H(21a) = 2.20 (2.37) and H(4)...H(5) = 2.39 (2.44) Å. The short contacts involving the C(20) and C(21) methyl groups force them out of the C(6)N(12)C(11) plane by 0.199 (4) (0.318) and 0.264 (4) (0.304) Å, respectively.

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Structures of Diazapolycyclic Compounds. IX. 1,3-Dimethyl-1,4-dihydrobenzo[*g*]pyridazino[1,2-*b*]phthalazine-6,13-dione

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Abstract. C₁₈H₁₆N₂O₂, $M_r = 292.33$, triclinic, $P\bar{1}$, $a = 11.2747$ (5), $b = 9.0849$ (2), $c = 7.7367$ (2) Å, $\alpha = 109.903$ (2), $\beta = 83.234$ (2), $\gamma = 108.492$ (3)°, $V = 706.62$ (4) Å³, $Z = 2$, $D_x = 1.37$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.692$ mm⁻¹, $F(000) = 308$, room temperature, 2396 unique reflections, $R = 0.050$. The pyrazine ring exhibits a distorted envelope conformation with N(14) at the flap. The methyl group bonded to C(1) occupies an axial position. As expected, the deformations in the amide groups are greater at the N atoms. The diazaquinone ring is nearly planar, with the O atoms out of this plane. All bond distances and angles, within the molecule, are normal.

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