

9-one, the former adopting the twin-chair and the latter the boat-chair conformation because of the different N...N lone-pair repulsions (McCabe, Milne & Sim, 1985).

The out-of-plane angle of the N-S bond in the title compound, 28.5°, is smaller than the N-C out-of-plane angle of 58.8° in cyclopropylamine (Rall, Harmony, Cassada & Staley, 1986) and 37.5° in aniline (Lister, Tyler, Høg & Larsen, 1974). The out-of-plane angle of the N-X bond in a molecule NX₃ with C_{3v} symmetry is related to the X-N-X angle by the equation

$$\varphi = \cos^{-1}[-\cos XNX/(\cos XNX/2)]^*$$

and in NH₃ where the H-N-H angle is 107.1° (Helminger, De Lucia & Gordy, 1971) the out-of-plane angle φ is 60.3°. In NMe₃ the C-N-C angle is ca 109° (Lide & Mann, 1958) and φ is therefore ca 56°. The shallower N pyramid in the arylsulfonamide is a consequence of some double-bond character in the N-S bond, 1.626 (2) Å.

I am grateful to the SERC for a grant towards the purchase of the diffractometer.

* For a molecule NX₂Y with C_s symmetry the appropriate expression for the angle between the N-Y bond and the X-N-X plane is

$$\varphi = \cos^{-1}[-\cos XNY/(\cos XNX/2)].$$

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Structure of N-Phenyl-5,6,7,8-tetrahydrobenzo[*a,i*]carbazole

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Abstract. C₂₆H₂₁N, *M_r* = 347.2, tetragonal, *P*4₁2₁2, *a* = 7.936 (1), *c* = 29.822 (3) Å, *V* = 1878.2 Å³, *Z* = 4, *D_x* = 1.229 Mg m⁻³, λ(Cu Kα) = 1.54178 Å, μ = 0.050 mm⁻¹, *F*(000) = 736, *T* = 298 K, final *R* = 0.041 for 976 observed reflections. The molecule has crystallographic twofold symmetry. The fused-ring system is non-planar, with the two halves inclined at an

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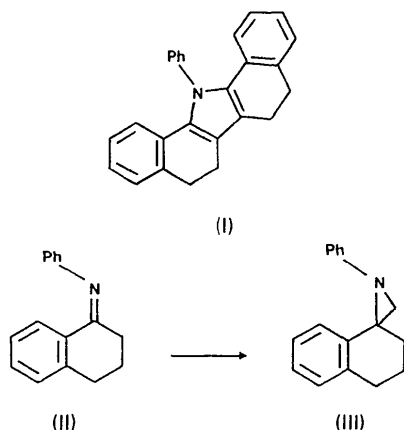
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angle of 30.3 (3)° along the twofold axis. The phenyl ring attached to the N atom is inclined at 112.1 (3)° to each half. The symmetry-equivalent tetrahydrobenzene rings have half-chair pucker.

Introduction. The title compound (I) was unexpectedly produced during the attempted synthesis of (III) from (II) by means of a carbene addition (Corey & Chaykovsky, 1962). A structural assignment was made

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by proton NMR analysis, and this was confirmed by an X-ray crystallographic study. Details of the chemistry will be reported elsewhere.



Experimental. Yellow prismatic crystals, 0.20 × 0.15 × 0.10 mm. CAD-4 diffractometer, cell dimensions from measurements on 25 reflections. $\omega/2\theta$ scan with Ni-filtered Cu $K\alpha$ radiation ($1.5 < \theta < 60^\circ$). Range of hkl : $0 \leq h \leq 8$, $0 \leq k \leq 8$, $0 \leq l \leq 32$. Three standards measured during data collection, no significant decomposition; 1288 unique reflections, 976 with significant [$I > 2\sigma(I)$] intensity. Structure solved with difficulty using *MULTAN80* (Main *et al.*, 1980) and Fourier-map recycling. Refinement using the *SDP* package (Enraf-Nonius, 1979), full-matrix least-squares refinement on F , with non-H atoms having anisotropic temperature factors and H atoms (located from a difference Fourier synthesis) having isotropic temperature factors. Absorption correction using program *DIFABS* (Walker & Stuart, 1983). Weights $w = 1/[\sigma^2(F_o) + 0.04(F_o)^2]$, final $R = 0.041$, $wR = 0.049$ maximum shift/e.s.d. in final least-squares cycle of 0.14, maximum and minimum peaks in final difference map of 0.3 and $-0.24 \text{ e } \text{\AA}^{-3}$ respectively. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and averaged isotropic temperature factors for the non-H atoms are given in Table 1,* bond lengths and angles in Table 2. The molecule lies on a crystallographic twofold axis which passes through atoms C1, C4 and N1 (Fig. 1). The symmetry-equivalent tetrahydrobenzene rings have approximate half-chair puckers; for each, atoms C12 and C13 deviate from the least-squares plane of C5,

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43641 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and averaged isotropic temperature factors for non-H atoms

	x	y	z	B(\AA^2)
N	0.2988 (3)	0.299	0.000	2.67 (4)
C1	0.6730 (4)	0.673	0.000	4.73 (7)
C2	0.6723 (4)	0.5513 (4)	-0.0324 (1)	4.29 (7)
C3	0.5505 (3)	0.4267 (4)	-0.03271 (9)	3.19 (6)
C4	0.4268 (3)	0.427	0.000	2.51 (5)
C5	0.2867 (3)	0.1657 (9)	0.03001 (9)	2.63 (5)
C6	0.4018 (3)	0.1173 (3)	0.06599 (8)	2.61 (5)
C7	0.5699 (4)	0.1664 (4)	0.07012 (9)	3.50 (6)
C8	0.6655 (4)	0.1130 (4)	0.1064 (1)	4.34 (7)
C9	0.5984 (4)	0.0084 (4)	0.1384 (1)	4.26 (6)
C10	0.43335 (4)	-0.0479 (4)	0.13373 (9)	3.56 (6)
C11	0.3353 (4)	0.0040 (4)	0.09812 (9)	3.08 (6)
C12	0.1535 (4)	-0.0522 (4)	0.09418 (9)	3.93 (6)
C13	0.965 (4)	-0.0782 (4)	0.0463 (1)	3.90 (6)
C14	0.1455 (3)	0.0732 (3)	0.01902 (9)	2.94 (5)

E.s.d.'s are in parentheses. The averaged isotropic thermal parameters are defined as $B = (B_{11}B_{22}B_{33})^{1/3}$.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

E.s.d.'s are in parentheses.			
C1-C2	1.365 (3)	C7-C8	1.387 (3)
C2-C3	1.383 (3)	C8-C9	1.373 (4)
C3-C4	1.384 (3)	C9-C10	1.390 (3)
C4-N1	1.437 (2)	C10-C11	1.380 (3)
N1-C5	1.388 (2)	C11-C12	1.514 (4)
C5-C6	1.461 (3)	C12-C13	1.513 (3)
C5-C14	1.379 (3)	C13-C14	1.501 (3)
C6-C7	1.396 (3)	C14-C14'	1.395 (3)
C6-C11	1.416 (3)		
C1-C2-C3	120.9 (2)	C12-C11-C10	120.6 (2)
C2-C3-C4	119.3 (2)	C10-C11-C6	120.0 (2)
C3-C4-N1	120.1 (1)	C12-C11-C6	119.3 (2)
C6-C5-N1	129.1 (2)	C11-C12-C13	113.5 (2)
C14-C5-N1	107.9 (2)	C12-C13-C14	108.9 (2)
C14-C5-C6	122.9 (2)	C13-C14-C5	120.5 (2)
C5-C6-C11	126.1 (2)	C5-N1-C4	126.0 (2)
C5-C6-C11	115.5 (2)	C2-C1-C2'	119.6 (2)
C11-C6-C7	118.3 (2)	C5-N1-C5'	108.0 (2)
C8-C7-C6	120.4 (2)	C3-C4-C3'	119.6 (2)
C9-C8-C7	121.0 (2)	C5-C14-C14'	108.0 (2)
C10-C9-C8	119.3 (2)	C13-C14-C14'	131.5 (2)
C11-C10-C9	120.8 (2)		

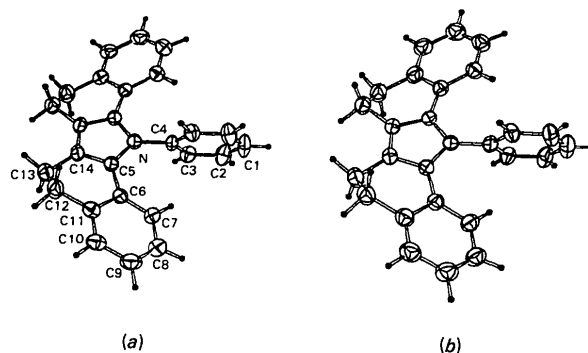


Fig. 1. The molecular structure of *N*-phenyl-5,6,7,8-tetrahydrobenzo[*a,i*]carbazole, with (a) observed and (b) calculated thermal ellipsoids drawn at the 50% probability level.

C6, C11, C14 by -0.378 (3) and 0.278 (3) Å respectively. The Cremer & Pople (1975) ring-pucker parameters Q , θ and φ have values of 0.45 Å, 67.3° and 85.6° , close to the standard half-chair values of $\theta = 51^\circ$, $\varphi = 90^\circ$.

The fused-ring system of the molecule is non-planar, with the two halves inclined at an angle of 30.3 (3)° along the twofold axis. The phenyl ring that is attached at atom N1 is inclined at 112.1 (3)° to each half.

The anisotropic thermal parameters obtained from the least-squares refinement were examined by the Hirshfeld (1976) test, which measures the differences in vibrational amplitude between bonded atoms. If the anisotropic parameters do genuinely represent vibrational ellipsoids, these differences should be small since bond-stretching vibrations have a much smaller amplitude than others. $\Delta\sigma\beta$ was defined as the root-mean-square of the differences in the mean-square vibrational amplitudes of bonded atoms along the directions of their bonds. $\Delta\sigma\beta$ was 0.00488 Å, indicating that the U_{ij} values were of good quality. Application of TLS rigid-body analysis (Schomaker & Trueblood, 1968) gave values of 0.160 and 0.00487 Å² for R_u and ΔU , defined respectively as $\sum |U_{ij}^o| - |U_{ij}^c| / \sum |U_{ij}^o|$ and $\langle (U_{ij}^o - U_{ij}^c)^2 \rangle^{1/2}$. These measures of agreement between observed and calculated thermal parameters indicate that the rigid-body approximation is fairly well obeyed. Fig. 1 shows the observed and calculated

models, drawn with ORTEP (Johnson, 1976). The main librational motion of the molecule, of 10.2 (°)², is along an axis that is roughly parallel to the planes of the fused rings, and perpendicular to the crystallographic twofold axis. The libration about this axis, of 3.9 (°)², is much less.

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Acta Cryst. (1987). **C43**, 782–784

Structure Cristalline du Dihydrogénométhylènediphosphonate d'Ammonium et de Thallium

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(Reçu le 19 juillet 1986, accepté le 12 novembre 1986)

Abstract. $2(\text{NH}_4)^+ \cdot \text{H}_2(\text{CH}_2\text{O}_6\text{P}_2)^{2-}$, $M_r = 210$, triclinic, $C\bar{1}$, $a = 13.197$ (17), $b = 7.910$ (7), $c = 8.097$ (3) Å, $\alpha = 94.00$ (6), $\beta = 113.64$ (8), $\gamma = 90.47$ (8)°, $V = 771$ Å³, $Z = 4$, $D_x = 1.81$ g cm⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 5.43$ cm⁻¹, $F(000) = 440$, room temperature, $R = 0.036$ for 2081 independent reflections. $2\text{Tl}^+ \cdot \text{H}_2(\text{CH}_2\text{O}_6\text{P}_2)^{2-}$, $M_r = 582.7$, triclinic, $C\bar{1}$,

$a = 12.786$ (4), $b = 7.936$ (3), $c = 8.385$ (2) Å, $\alpha = 95.55$ (3), $\beta = 113.69$ (2), $\gamma = 90.28$ (4)°, $V = 774$ Å³, $Z = 4$, $D_x = 4.99$ g cm⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 423.7$ cm⁻¹, $F(000) = 1000$, room temperature, $R = 0.086$ for 2629 independent reflections. The crystal structure can be regarded as being built up of infinite chains of MDP linked together by M^+ ions.