

Discussion. The crystal structure contains discrete molecules of the *cis* isomer linked in chains parallel to *c* by intermolecular O(4)—H...O(1) (2.703 Å) hydrogen bonds (Fig. 1). The conformation of the carboxyl groups allows the formation of an intramolecular hydrogen bond [O(2)—H...O(3) 2.827 Å]. In each aromatic ring the atoms are close to coplanar (r.m.s. deviation 0.003–0.006 Å). The furan ring is slightly distorted from planarity towards a very shallow envelope conformation with O(5) 0.031 Å from the five-membered-ring plane; the dihedral angle between the furan- and benzene-ring planes in the isobenzofuran moiety is 2.0°. The orientations of the phenyl and carboxylic groups are defined by the torsion angles C(11)—C(1)—C(21)—C(22) –13.8, C(12)—C(3)—C(31)—C(36) 25.4, C(11)—C(1)—C(2)—O(1) –79.8, and C(12)—C(3)—C(4)—O(3) –98.4°. The bond lengths in the molecule are in accord with expected values; mean distances are C(sp²)—C(sp²) aromatic

1.382, C(sp²)—C(sp³) 1.525, C(sp³)—O 1.444, C=O 1.208, C(sp²)—O 1.309 Å.

We thank Dr J. G. Smith for bringing the problem to our attention. Financial support from the National Research Council of Canada is gratefully acknowledged.

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Acta Cryst. (1979). **B35**, 1722–1724

Benzo[*b*][1,4]diazabicyclo[3.2.1]octane, a Molecule Containing a \dot{N} —C(sp²) Single Bond

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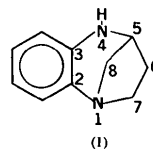
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(Received 1 November 1978; accepted 21 March 1979)

Abstract. C₁₀H₁₂N₂, *M_r* = 160.2, monoclinic, *P*2₁/*n*, *a* = 9.764 (6), *b* = 10.528 (2), *c* = 8.698 (2) Å, β = 106.31 (2)°, *Z* = 4, *D_c* = 1.24 Mg m⁻³. The structure was solved with direct methods. The final *R* index was 0.037 for 1041 reflections. The two benzene— \dot{N} bonds are, respectively, 1.387 and 1.452 Å. The first is typical of anilines and reflects some double-bond character, whereas the geometry of the nitrogen involved in the 1.452 Å bond indicates that it is essentially a single \dot{N} —C(sp²) linkage.

Introduction. Our initial interest in the title compound (I) was as a bridgehead N-containing substrate for lanthanide shift reagent—nuclear magnetic resonance experiments. Its structural details were of interest because the orientations of the secondary [N(4)] and tertiary [N(1)] nitrogen atoms relative to the aromatic ring suggest that two quite different amine—C(sp²) bonds are present in the molecule. In particular, N(1)'s non-bonding electron-pair orbital should be approximately parallel to the adjacent benzene ring, resulting in

a situation in which the N(1)—C(2) bond should be essentially free of bond-shortening π-type conjugation effects.



(I) was prepared according to the procedure of Cunningham (1969) and Cunningham & Day (1973) with modifications: colorless solid, m.p. 407–408 K (literature m.p. 404–407 K). Recrystallization from petroleum ether (333–383 K) gave suitable diffraction samples. All X-ray measurements were made with a 0.2 × 0.2 × 0.4 mm specimen mounted parallel to the long crystal axis (*b*) on a Picker FACS-I diffractometer with Mo radiation (graphite monochromator, *K*α, λ = 0.71069 Å). The unit-cell parameters were obtained by least squares from the Bragg angles of 13 reflections manually centered at ±2θ (average of |2θ_o – 2θ_c| = 0.004°).

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X-ray intensities were measured with the θ - 2θ scan method with a 2θ rate of 2° min^{-1} and with 10 s backgrounds. Three standard reflections were counted at 100-reflection intervals. 1762 data were measured to a 2θ maximum of 50° giving 1513 unique reflections (excluding 98 systematically absent data); 1041 of these were 3σ above background. The structure was solved by the routine application of direct methods with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) subprogram PHASE. An E map computed with 244 phases (116 +, 128 -) revealed the twelve C and N atoms. The structure was refined by the full-matrix least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1$ for $F_o < 12$ and $w = (12/F_o)^2$ for $F_o > 12$ (Hughes, 1941). The calculations used anisotropic temperature factors for C and N, isotropic terms for H (preliminary H positions were calculated from the geometry of the C-N framework) and included a correction for isotropic extinction

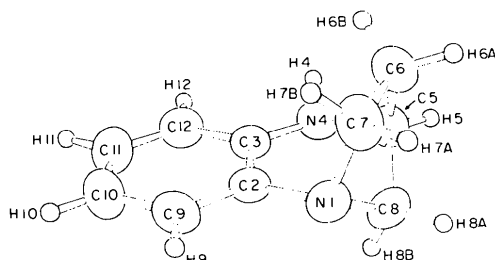


Fig. 1. ORTEP drawing (Johnson, 1965). The C and N atoms are depicted as 50% ellipsoids, and the H atoms are drawn as 0.1 Å radius circles.

Table 1. Atomic fractional coordinates and estimated standard deviations (in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.7895 (2)	0.2018 (1)	0.3572 (2)
N(4)	0.9977 (2)	0.3039 (2)	0.6204 (2)
C(2)	0.8008 (2)	0.1593 (2)	0.5191 (2)
C(3)	0.9085 (2)	0.2091 (2)	0.6475 (2)
C(5)	0.9922 (2)	0.3271 (2)	0.4536 (2)
C(6)	1.0403 (2)	0.2136 (2)	0.3720 (3)
C(7)	0.9020 (2)	0.1389 (2)	0.2992 (3)
C(8)	0.8352 (2)	0.3357 (2)	0.3636 (3)
C(9)	0.7087 (2)	0.0682 (2)	0.5459 (3)
C(10)	0.7222 (2)	0.0221 (2)	0.6986 (3)
C(11)	0.8293 (3)	0.0701 (2)	0.8246 (3)
C(12)	0.9196 (2)	0.1630 (2)	0.8012 (2)
H(4)	1.088 (3)	0.304 (2)	0.693 (3)
H(5)	1.047 (2)	0.405 (2)	0.450 (2)
H(6A)	1.081 (2)	0.243 (2)	0.288 (3)
H(6B)	1.113 (2)	0.165 (2)	0.451 (3)
H(7A)	0.871 (2)	0.147 (2)	0.184 (3)
H(7B)	0.908 (2)	0.047 (2)	0.328 (3)
H(8A)	0.822 (2)	0.368 (2)	0.254 (3)
H(8B)	0.780 (2)	0.389 (2)	0.418 (3)
H(9)	0.635 (2)	0.038 (2)	0.456 (3)
H(10)	0.659 (2)	-0.043 (2)	0.717 (3)
H(11)	0.839 (2)	0.036 (2)	0.933 (3)
H(12)	0.994 (2)	0.196 (2)	0.891 (3)

(Larson, 1970). Reflections were included in the refinement only if $I_o > 3\sigma(I_o)$. Atomic scattering factors for C and N were calculated from the analytical expressions of Cromer & Mann (1968); the H scattering factors were interpolated from the tabulated values of Stewart, Davidson & Simpson (1965). The final R ($\sum |F_o| - |F_c| / \sum |F_o|$) and weighted R ($\{\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2\}^{1/2}$) values were 0.037 and 0.044 respectively. Atomic coordinates are listed in Table 1.*

Discussion. An ORTEP drawing of (I) is shown in Fig. 1. The benzene ring is planar within experimental error with average and maximum out-of-plane deviations of 0.006 and 0.010 Å, and both nitrogen substituents are close to the plane with out-of-plane deviations of 0.068 Å [N(1)] and -0.029 Å [N(4)]. The N(1)-C(7)-C(6)-C(5) bridge is approximately planar with average and maximum out-of-plane deviations of 0.031 and 0.038 Å.

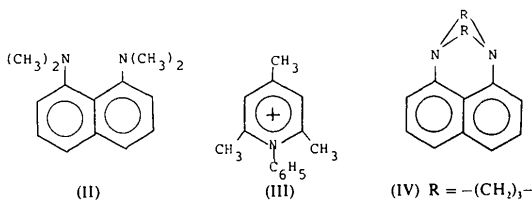
Bond lengths and angles are listed in Table 2. The extent to which the sum of the bond angles at a tri-substituted atom differs from 360° can provide a measure of the planarity of the atom. The angle sum of 346° at the secondary nitrogen N(4), while significantly different from 360° , is within the bounds of what one would expect for a planar atom in conjugation with an adjacent benzene ring. The C(3)-N(4) distance of 1.387 Å is typical of aniline-type C-N bonds and reflects some double-bond character. In 1,8-bis-

* Lists of structure factors, thermal parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34286 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), and bond angles ($^\circ$), with estimated standard deviations in parentheses, for the carbon and nitrogen atoms

N(1)-C(2)	1.452 (2)	N(4)-C(5)	1.457 (3)
N(1)-C(7)	1.486 (3)	C(5)-C(6)	1.529 (3)
N(1)-C(8)	1.475 (3)	C(5)-C(8)	1.515 (3)
C(2)-C(3)	1.403 (3)	C(6)-C(7)	1.537 (3)
C(2)-C(9)	1.378 (3)	C(9)-C(10)	1.385 (3)
C(3)-N(4)	1.387 (2)	C(10)-C(11)	1.380 (3)
C(3)-C(12)	1.398 (3)	C(11)-C(12)	1.370 (3)
C(2)-N(1)-C(7)	109.2 (1)	N(4)-C(5)-C(8)	105.9 (2)
C(2)-N(1)-C(8)	108.5 (1)	C(6)-C(5)-C(8)	101.8 (2)
C(7)-N(1)-C(8)	101.2 (2)	C(5)-C(6)-C(7)	104.0 (2)
N(1)-C(2)-C(3)	119.5 (2)	N(1)-C(7)-C(6)	106.2 (2)
N(1)-C(2)-C(9)	120.2 (1)	N(1)-C(8)-C(5)	102.3 (2)
C(3)-C(2)-C(9)	120.3 (2)	C(2)-C(9)-C(10)	121.0 (2)
C(2)-C(3)-N(4)	120.0 (2)	C(9)-C(10)-C(11)	118.7 (2)
C(2)-C(3)-C(12)	118.1 (2)	C(10)-C(11)-C(12)	121.3 (2)
N(4)-C(3)-C(12)	121.9 (2)	C(3)-C(12)-C(11)	120.6 (2)
C(3)-N(4)-C(5)	116.1 (1)		
N(4)-C(5)-C(6)	113.7 (2)		

(dimethylamino)naphthalene (II), for example, *peri* interactions have forced one CH₃ of each (CH₃)₂N group out of the naphthalene plane, resulting in angle sums at both nitrogens of 347°; the average C(naphthalene)—N distance is 1.397 Å and the amount of π character in these bonds has been estimated at 20% (Einspahr, Robert, Marsh & Roberts, 1973). In the case of the tertiary nitrogen atom N(1), the angle sum of 318.4° clearly indicates a pyramidal geometry, and the arrangement of C(7) and C(8), respectively, above and below the benzene plane, suggests that the usual C(sp²)—N(amine) π -type conjugation must be minimal for C(2)—N(1). This possibility is supported by the 1.452 Å distance, which undoubtedly is close to that of a single C(sp²)—N(sp³) bond. Other C—N distances which provide points of reference are the C(sp³)—N(sp³) of 1.472 Å in methylamine (Sutton, 1965), the presumably pure single bond C(sp²)—N(sp²) of 1.470 Å in (III) (Camerman, Jensen & Balaban, 1969; Camerman, 1970), and the 1.425 Å in (IV) (Adler, Goode, King, Mellor & Miller, 1976), which might be classified as C(sp²)—N(sp²) based on the average angle sum of 356° at nitrogen. The difference between the C(sp²)—N(sp²) lengths in (III) and (IV) is presumably due to the different kinds of nitrogen atoms (\ddot{N} vs N⁺).



The intermolecular packing arrangement is limited to van der Waals contacts, with one exception. There is a weak N(4)—H(4)···N(1) interaction (2.08 Å) between

the N acceptor at x, y, z and the H donor at $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

This work was supported by the National Institutes of Health (R01-AM17458). The crystallographic calculations were supported through the facilities of the Computer Science Center, University of Maryland.

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Acta Cryst. (1979). **B35**, 1724–1727

Structure of Adenosine 5'-Methylphosphonate Hemihydrate

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(Received 8 November 1978; accepted 4 April 1979)

Abstract. C₁₁H₁₆N₅O₆P·½H₂O, P1, $a = 10.510$ (2), $b = 9.419$ (2), $c = 7.803$ (2) Å, $\alpha = 76.77$ (1), $\beta = 97.24$ (2), $\gamma = 95.99$ (1)°, $Z = 2$, $D_c = 1.582$, $D_o = 1.576$ Mg m⁻³, $V = 743.7$ Å³, $FW = 354.3$, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $T = 299 \pm 1$ K, $F(000) = 370$. The intensity data were collected on an automated diffractometer, and the structure was solved from a

0567-7408/79/071724-04\$01.00

sharpened Patterson function calculated with ($E^2 - 1$) coefficients. Full-matrix least-squares refinement of the 47 non-hydrogen atoms and difference Fourier placement of the 34 H atoms yielded an R of 0.029 for the 3339 significant data. The molecules are packed in pairs by base stacking and hydrogen bonds between the base and the phosphonate O atoms.

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