

Table 3. *Least-squares plane for the Cu₄Cl₁₀²⁻ tetramer in [(CH₃)₃NH]₂Cu₄Cl₁₀*

The equation of the plane is

$$0.4909x + 0.8712y - 0.0006z - 3.8238 = 0.$$

Atom	Distance from plane (Å)
Cu(1)	-0.142
Cu(2)	0.124
Cl(1)	0.101
Cl(2)	-0.066
Cl(3)	-0.230
Cl(4)	0.120
Cl(5)	0.046

(3.604 Å) are just equal to the sum of the van der Waals radii. The stacking is such that Cu(2) assumes a 4+1 coordination geometry, while Cu(1) takes on a 4+1+1 geometry. For the Cu(1) ion, the axial bond lengths are significantly different [Cu-Cl(4) 2.749, Cu-Cl(2) 3.225 Å] and the coordination geometry shows a pronounced square-pyramidal type distortion as indicated by the Cl(eq)-Cu(1)-Cl(ax) bond angles [average Cu(eq)-Cu(1)-Cl(4), 93.8 Å] and the *trans* Cl(eq)-Cu(1)-Cl(eq) angles (average 172.4°). For Cu(2) the distortion of the CuCl₄²⁻ moiety is more complex, with Cu(2), Cl(1), Cl(2) and Cl(4) being approximately coplanar and the Cu(2)-Cl(3) bond being tipped about 14° out of this plane away from the axial ligand.

The three unique bridging Cu-Cl-Cu bond angles average 94.2°, but are individually 93.2, 94.1 and 95.2°. Thus if, as has been proposed (Willett, 1973), this bridging angle controls the sign and magnitude of the magnetic exchange interaction, the Cu(1)-Cu(1) interaction should be ferromagnetic, but the interaction between Cu(1) and Cu(2) will probably be anti-ferromagnetic. Attempts to characterize the magnetic properties of this system have been frustrated by the difficulty of obtaining bulk samples free from CuCl₂ contamination.

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Dibenzo-1,3a,4,6a-tetraazapentalene

BY MARY BURKE LAING,* ROBERT A. SPARKS,† MICHAEL J. LAING* AND K. N. TRUEBLOOD
Department of Chemistry,‡ University of California, Los Angeles, California 90024, U.S.A.

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Abstract. C₁₂H₈N₄, monoclinic, *C2/c*, *a*=12.05 (1), *b*=5.541 (5), *c*=14.71 (1) Å, β=97.69 (10)°, *Z*=4, *D_c*=1.421, *D_x*=1.425 g cm⁻³ (by flotation). The structure was determined from packing considerations by a computer search, and was refined by least squares to *R*=0.09 (photographic data). The molecule is planar and the bond distances are in good accord with the predictions of Hückel molecular orbital theory.

Introduction. Yellow needles grown from a 1:1 mixture of CHCl₃ and CCl₄ were supplied by Dr R. A. Carboni. Unit-cell dimensions were obtained from photographs

calibrated with superimposed CeO₂-powder photos (*a*=5.411 Å), taken with Cu *Kα* radiation (λ=1.5418 Å). The systematic absences, *hkl* with (*h+k*) odd and *h0l* with *l* odd, indicated the space group to be *Cc* or *C2/c*; the structure analysis showed the latter to be correct. Intensities were measured visually and photometrically from integrated equi-inclination Weissenberg photographs taken with Ni-filtered Cu *Kα* radiation. Of the 1027 independent reflections within the Cu *Kα* sphere, 751 were observed, 182 were too weak to be measured, and 94 were inaccessible.

The approximate orientational parameters of the planar centrosymmetric molecule were found by a computer analysis of the positions of rigid assumed models situated at each of the two unique centers of symmetry of the presumed space group, *C2/c*, the origin and (¼, ¼, 0), very much as described earlier for an-

* Present address: 61 Baines Road, Durban, South Africa.

† Present address: Syntex Analytical Instruments, 10040 Bubb Road, Cupertino, California 95014, U.S.A.

‡ Contribution No. 1726.

other structure (Long, Sparks & Trueblood, 1965). The model was rotated in 3° steps about each of 300 different vectors in each of the two unique octants of the unit cell. More than 99% of the resulting possible structures gave too short intermolecular contacts and were rejected; discrimination among the remainder was done by comparison of *R* values for low-angle reflections. The entire analysis took only about 50 min on an IBM 7090. In retrospect, the grid could probably have been significantly coarser; although the correct structure corresponded to the lowest *R* value, a number of others with comparable *R* were sufficiently close that they doubtless would also have refined to the same solution.

The structure was refined by full-matrix least squares to *R*=0.115, at which point the four unique H atoms were found clearly on a difference Fourier synthesis. An empirical isotropic extinction correction was applied because some of the strongest reflections appeared markedly affected. Refinement of the atomic positions, anisotropic thermal parameters for the heavy atoms, and isotropic thermal parameters for the H atoms, converged after three more cycles to *R*=0.092 for all reflections, including the unobserved.* Hughes's

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31771 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

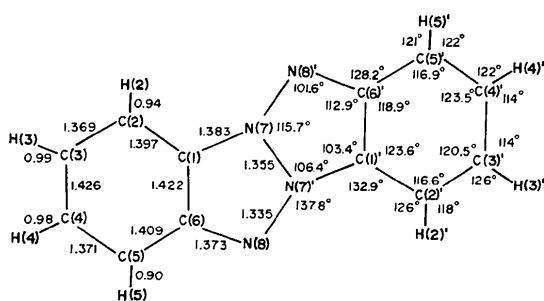


Fig. 1. Bond angles and distances, corrected for rigid-body molecular motion.

(1941) weighting scheme was used throughout. Scattering factors for C and N were from *International Tables for X-ray Crystallography* (1962) and that for H was from Stewart, Davidson & Simpson (1965). The final parameters are listed in Table 1.

Interatomic bond distances and angles are presented in Fig. 1; they have been corrected for rigid-body thermal motion (Cruickshank, 1956), the maximum correction to a bond distance being 0.004 Å. The e.s.d.'s are 0.004–0.006 Å for the N–N, N–C, and C–C bonds, 0.05–0.08 Å for the C–H bonds, 0.3–0.4° for the bond angles involving only heavy atoms, and 3–4° for the C–C–H angles. The molecule is planar within experimental error; the equation for the least-squares plane of the 16-atom molecular skeleton is $-0.0973X - 0.6017Y + 0.7928Z + 1.127 \text{ Å} = 0$, where *X*, *Y*, and *Z* are coordinates (in Å) measured parallel to *a*, *b*, and *c**.

Discussion. This heteroaromatic molecule (Carboni & Castle, 1962) is unusually stable when compared with others of similar nitrogen content. Because the four N atoms contribute six electrons to the π -electron system, the molecule is analogous to the dibenzopentalene dianion, and although dibenzopentalene itself exhibits distinct olefinic properties (Blood & Linstead, 1952), the title compound is stable to permanganate, can be recovered unchanged from solution in concentrated sulfuric acid, and can be heated in solvents to above 300°C without change.

The general pattern of distances in the molecule is in good accord with the predictions of Hückel molecular orbital theory (Table 2). The N–N bond across the center of symmetry has significantly lower double-bond character than the other unique N–N bond. This observation is consistent with the different resonance structures that one can write for the molecule; that with a double bond in this position has two adjacent formally positive N atoms, so its contribution is expected to be small. The HMO calculations indicate that N(7) has a charge of about +0.38 and N(8) a charge of about –0.33.

Despite the significant charge density on the N atoms there are no unusually close intermolecular distances between oppositely charged N atoms. The molecules

Table 1. Final positional and thermal parameters

All values $\times 10^4$ for C and N atoms; for H atoms, position parameters $\times 10^3$. Isotropic *B*'s for H atoms in Å²; for other atoms* the expression is $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{23}kl - b_{13}hl)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁ or <i>B</i>	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₂₃	<i>b</i> ₁₃
C(1)	2324 (3)	4914 (7)	682 (2)	63 (3)	254 (19)	33 (2)	–24 (8)	10 (7)	10 (3)
C(2)	1710 (3)	6633 (8)	1095 (3)	58 (3)	341 (20)	39 (2)	30 (9)	32 (8)	13 (3)
C(3)	2311 (4)	8320 (8)	1633 (3)	81 (4)	295 (21)	40 (2)	40 (10)	–1 (8)	20 (4)
C(4)	3501 (4)	8304 (8)	1738 (3)	80 (3)	289 (20)	41 (2)	–5 (10)	–4 (8)	2 (4)
C(5)	4113 (3)	6638 (8)	1330 (3)	60 (3)	336 (21)	45 (2)	–28 (10)	19 (8)	10 (4)
C(6)	3511 (3)	4863 (8)	785 (2)	60 (3)	314 (19)	35 (2)	–3 (9)	17 (7)	13 (3)
N(7)	2019 (2)	3006 (7)	96 (2)	38 (2)	315 (17)	38 (2)	8 (7)	24 (6)	10 (2)
N(8)	3921 (2)	3034 (7)	298 (2)	42 (2)	327 (17)	44 (2)	–22 (7)	0 (7)	4 (3)
H(2)	93 (6)	666 (12)	107 (4)	7.2 (1.7)					
H(3)	199 (5)	965 (11)	197 (4)	5.5 (1.2)					
H(4)	385 (5)	959 (11)	213 (4)	5.4 (1.2)					
H(5)	486 (4)	667 (8)	139 (3)	3.9 (1.0)					

Table 2. Comparison of observed bond distances and those predicted from molecular orbital theory

The parameters used were essentially self-consistent: $\alpha_{N(7)} = \alpha_C + 1.7\beta$; $\alpha_{N(8)} = \alpha_C + 0.4\beta$; $\beta_{C-C} = \beta_{C-N(7)} = 1.0$; $\beta_{C-N(8)} = \beta_{N-N} = 0.8$ (see also Chia & Simmons, 1967).

Bonds	π -Bond order	Predicted distance*	Observed distance
C(1)–C(6)	0.53	1.42 Å	1.42 Å
C(1)–C(2)	0.59	1.41	1.40
C(5)–C(6)	0.57	1.41	1.41
C(2)–C(3)	0.70	1.39	1.37
C(4)–C(5)	0.71	1.39	1.37
C(3)–C(4)	0.61	1.41	1.43
C(1)–N(7)	0.44	1.39	1.38
C(6)–N(8)	0.54	1.37	1.37
N(8)–N(7')	0.41	1.34	1.34
N(7)–N(7')	0.29	1.36	1.36

* From an empirical curve through points corresponding to graphite, benzene, and ethylene and the relation $r_N = r_C - 0.045 \text{ Å}$.

pack in interleaving sets of parallel planes (Fig. 2), as do many planar aromatic molecules. The distance between the planes of molecules in any one stack is 3.33 Å, comparable to the interlayer distance in graphite. The stacks run parallel to **b**, with the normals to the molecular planes inclined at about 53° to that axis; the angle between the normals to molecules in adjacent stacks is 74°. The shortest contact between stacks is from H(2) to N(8) of a molecule related by the C-centering operation, 2.64 Å, a distance only slightly (if at all) below the sum of the van der Waals radii. Although the C(2)–H(2)···N(8) angle is 165° and N(8) does bear some negative, the C(2)···N(8) distance is 3.49 Å and it does not seem meaningful to refer to this contact as a hydrogen bond. In addition, H(3) points toward the center of the six-carbon ring of a molecule [situated at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$] in an adjacent stack, approaching C(3) and C(4) of that molecule within about 2.9 Å. This type of contact is common in aromatic structures (see, for example, Gantzel & Trueblood, 1965; Shefter, Barlow, Sparks & Trueblood, 1969; and references cited therein).

A second monoclinic crystal form of this compound, with a density about 2% lower, has been found and its structure has been determined, although not refined to high precision (Laing, 1965). It forms crystals in space group $P2_1/c$, with $a_0 = 6.97$, $b_0 = 4.49$, $c_0 = 16.11 \text{ Å}$, $\beta = 100.25^\circ$, and $Z = 2$. The general mode of packing in this second modification is similar to that reported here.

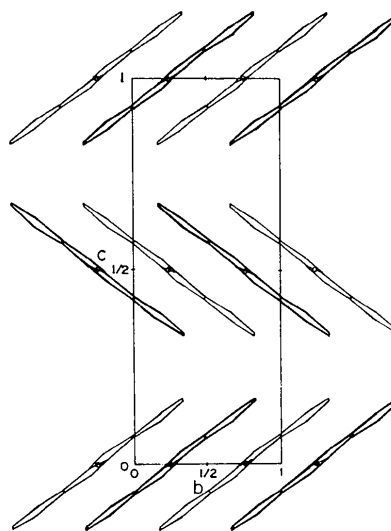


Fig. 2. A view of the structure along the $-a$ direction.

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