Betty R. Deroski

Department of Chemistry, Suffolk County Community College,
Seldon, NY 11784

J. Hodge Markgraf*

Department of Chemistry, Williams College,
Williamstown, MA 01267

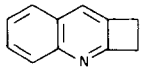
John S. Ricci, Jr. [2]

Departments of Chemistry, Williams College, Williamstown, MA 01267
and Brookhaven National Laboratory, Upton, NY 11973
Received August 30, 1982

The structure of the title compound (**1**) has been elucidated by an X-ray crystal determination. The crystals are triclinic, space group $P\bar{1}$ with a unit cell of dimensions a = 6.6109(5), b = 7.5939(4), c = 9.3171(6), α = 77.133(5), β = 75.566(6), γ = 63.575(5). The model was refined to an R value (unweighted) of 4.3% for 1551 independent reflections. The distortion of the heterocyclic ring, with a CNC bond angle of 112.5°, is in accordance with a prior calculation and relates to the observed reduction in basicity.

J. Heterocyclic Chem., **20**, 1155 (1983).

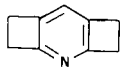
Some years ago we first reported that a fused, strained ring adjacent to the nitrogen atom of quinoline caused a reduction in basicity [3]. The initial studies on 1,2-dihydrocyclobuta[*b*]quinoline (**1**) were extended by us and others to a variety of related heterocyclic systems [4-9]. The most



1

notable recent work has been that of Thummel and co-workers who have reported the synthesis and basicities of strained pyridines **2** and **3** [8,9]. The observed effect of

2



3

ring strain on basicity has been interpreted in terms of orbital rehybridization, whereby the bridgehead carbon at the ring fusion uses orbitals with enhanced p character in bonding to the small ring [10]. Such rehybridization results in an orbital of higher s character to bond with the adjacent nitrogen. As a consequence of such an induced effect, the nonbonding (n) electron pair on nitrogen is in an orbital of higher s character and thus is less available as a proton acceptor. Consistent with this interpretation is the absence of diminished basicity when the small ring is fused to other than the [*b*] face of pyridine [7,8] and quinoline [11].

Very recently, however, the geometry of the heterocyclic ring has been identified as the major factor in determining the proportion of s-character of the n orbital [1]. Molecular orbital calculations, using the partial retention of diatomic differential overlap (PRDDO) approximation [12], showed that the percent s-character of the nonbonding orbital was increased more by smaller C(2a)-N(3)-C(3a) angles than by changes in the hybridization of the carbons at the ring fusion. Furthermore, partial geometry optimization of **1** gave a CNC angle of 112.1°, a value markedly smaller than that observed for any cyclobutanaphthalene system (*vide infra*). These results prompted us to submit this compound to crystallographic X-ray analysis.

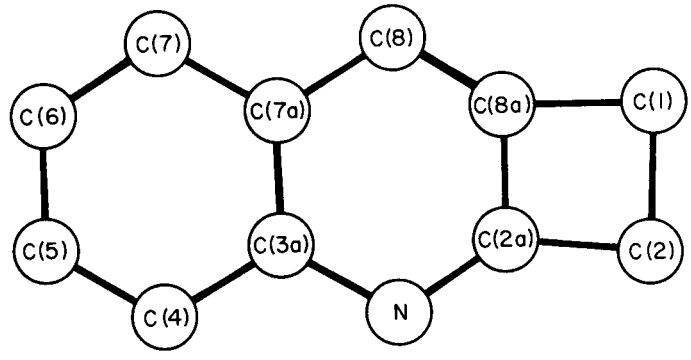


Figure 1. Diagram of 1,2-dihydrocyclobuta[*b*]quinoline with atomic numbering.

EXPERIMENTAL

Crystal Data.

Crystals of **1** [13], $C_{11}H_9N$, are triclinic, space group $P\bar{1}$, a = 6.6109(5), b = 7.5939(4), c = 9.3171(6), α = 77.133(5), β = 75.566(6), γ = 63.575(5); V = 402.27 Å^3 (λ = CuK$_\alpha$ = 1.5418 at 18°C); Z = 2; D_{Calcd} = 1.28 g/cm^3; absorption coefficient, μ(CuK$_\alpha$) = 5.918 cm^{-1}.

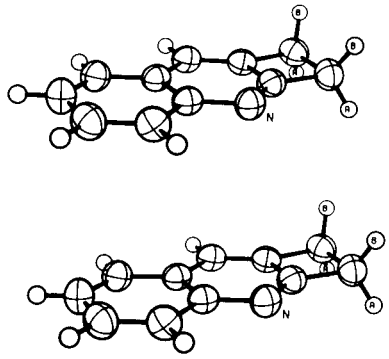


Figure 2. The molecule shown with 50% probability ellipsoids; A refers to H(1A) and H(2A) and B to H(1B) and H(2B).

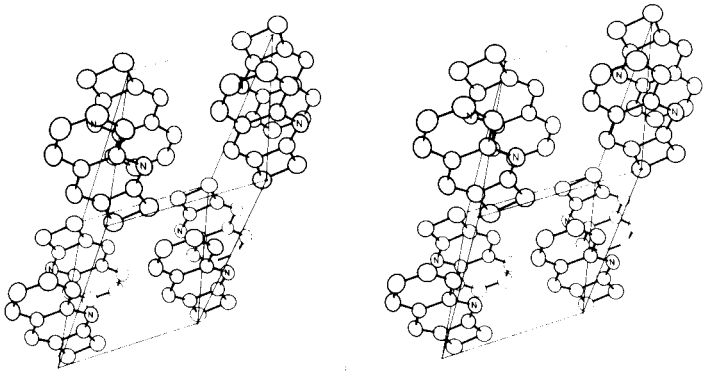


Figure 3. The unit cell.

Data Collection.

Precession photographs and cell reduction calculations revealed the crystal to be triclinic. The cell dimensions were determined by a least-squares fit of the observed 2θ angles for 24 reflections centered automatically.

Three dimensional intensity data were measured on a computer-controlled Enraf-Nonius CAD-4 diffractometer using CuK_α radiation monochromatized by reflection from a highly ordered graphite monochromator. The data crystal of 0.50(010) × 0.42(100) × 0.19(001) mm was clear, air stable, and mounted along the crystallographic (111) direction. Data were collected by $\theta - 2\theta$ scans to $2\theta(CuK_\alpha) = 154°$ ($\sin\theta/\lambda = 0.63$). Peak backgrounds were measured as one-tenth of the total scan width (0.7°) on each side. Normal scans which did not result in sufficiently high precision on net intensity measurements were repeated at a slower scan speed. The take-off angle was 3.2° and the diffracted beam was automatically corrected for coincidence losses. One form of data yielding 1736 unique reflections was collected. These were scaled to standards (decomposition = 18%) and corrected for absorption using BNLABS, a local version of ORABS [14]. The absorption corrections to F_o^2 ranged from 0.76 to 0.90.

Solution of the Structure.

An earlier data set consisting of very weak intensities (MoK_α radiation, small crystal) had been collected on this material. Using these data, direct method techniques failed to yield a successful solution. The orientation of the ten-membered ring was located by Patterson techniques by which peaks were correlated with ring centers from which in turn carbon atom positions were calculated. The remaining carbon atom positions were located in an observed Fourier and the position of the nitrogen atom was determined on the basis of isotropic thermal parameters. Although these data did not yield a successful refinement, these positional parameters were those used as input to the current data refinement.

Refinement.

The nitrogen and eleven carbon atoms were refined by differential synthesis refinement [15]. At this point the nine hydrogen atoms were

Table 1

Positional Parameters (× 10^4), Anisotropic Thermal Parameters (× 10^4), and Isotropic Thermal Parameters With Estimated Standard Deviations in Parentheses [a]

Atom	x	y	z	β_{11} or β	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(3)	1672(2)	2211(1)	884(1)	229(3)	219(2)	116(1)	−102(2)	−39(1)	−21(1)
C(2a)	1535(2)	2326(2)	−511(1)	242(3)	175(2)	114(2)	−89(2)	−33(2)	−16(1)
C(8a)	−346(2)	2567(2)	−1100(1)	275(4)	178(2)	107(1)	−94(2)	−49(2)	−10(1)
C(8)	−2356(2)	2731(2)	−192(1)	247(3)	198(3)	121(2)	−94(2)	−64(2)	−9(1)
C(7)	−4378(2)	2856(2)	2436(1)	236(3)	226(3)	138(2)	−102(3)	−34(2)	−16(2)
C(6)	−4383(2)	2780(2)	3916(2)	291(4)	270(3)	130(2)	−120(3)	7(2)	−30(2)
C(5)	−2395(2)	2485(2)	4395(1)	360(5)	267(3)	108(2)	−131(3)	−29(2)	−23(2)
C(4)	−430(2)	2283(2)	3388(1)	297(4)	238(3)	113(2)	−117(3)	−54(2)	−18(2)
C(3a)	−363(2)	2384(2)	1845(1)	230(3)	170(2)	108(1)	−81(2)	−43(2)	−15(1)
C(7a)	−2381(2)	2658(2)	1358(1)	223(3)	163(2)	115(2)	−78(2)	−41(2)	−14(1)
C(2)	3082(2)	2254(2)	−2020(1)	298(4)	234(3)	120(2)	−120(3)	−7(2)	−29(2)
C(1)	981(2)	2528(2)	−2687(1)	348(4)	225(3)	107(2)	−123(3)	−36(2)	−15(2)
H(8)	−3802(28)	2922(22)	−521(17)	4.9(3)					
H(7)	−5713(29)	3021(23)	2071(20)	5.8(4)					
H(6)	−5780(33)	2921(25)	4629(21)	6.3(4)					
H(5)	−2439(30)	2457(24)	5471(19)	6.5(4)					
H(4)	992(29)	2061(24)	3739(20)	5.8(4)					
H(2A)	4417(26)	992(21)	−2112(16)	5.1(3)					
H(2B)	3529(26)	3395(22)	−2312(17)	4.9(3)					
H(1A)	1190(24)	1430(20)	−3186(16)	4.7(3)					
H(1B)	276(25)	3858(21)	−3359(17)	5.4(3)					

[a] Anisotropic thermal parameters in the form $\exp[-\beta_{11}k^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]$.

Table 2

Interatomic Distances With Estimated Standard Deviations in Parentheses

Bond	Length (Å)
N(3)-C(2a)	1.307(1)
N(3)-C(3a)	1.387(1)
C(2a)-C(8a)	1.405(2)
C(2)-C(2a)	1.514(2)
C(8)-C(8a)	1.355(2)
C(1)-C(8a)	1.518(2)
C(7a)-C(8)	1.429(2)
C(6)-C(7)	1.366(2)
C(7)-C(7a)	1.416(2)
C(5)-C(6)	1.401(2)
C(4)-C(5)	1.368(2)
C(3a)-C(4)	1.414(2)
C(3a)-C(7a)	1.429(2)
C(1)-C(2)	1.573(2)
C(8)-H(8)	1.02(2)
C(7)-H(7)	.97(2)
C(6)-H(6)	.97(2)
C(5)-H(5)	.99(1)
C(4)-H(4)	1.00(2)
C(2)-H(2A)	.98(1)
C(2)-H(2B)	.97(1)
C(1)-H(1A)	.98(1)
C(1)-H(1B)	1.04(1)

located by a difference Fourier synthesis as the nine highest peaks in the map. Atomic scattering factors were taken from a standard source [16], while that for hydrogen was the best spherically averaged value of Stewart, *et al.* [17]. In the final least-squares calculations, the function minimized was $\Sigma\omega\Delta^2$, where $\Delta = |F_o| - |F_c|$ with weights $\omega = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2_{count}(I) + (0.03F^2)^2$. Using a three sigma rejection, 1551 reflections were included in the refinement. All non-hydrogen atoms were allowed to vary anisotropically, hydrogen atoms isotropically, and extinction isotropically to give values of $R_1 = 0.043$ and $R_2 = 0.068$ where $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_2 = \{[\Sigma W\|F_o| - |F_c\|^2]/\Sigma W|F_o|^2\}^{1/2}$. The extinction coefficient was refined to 0.42 with the 100 reflection requiring the maximum correction (0.75). The error in an observation of unit weight was 3.28. The maximum density in a final difference Fourier was 0.19 electron $Å^{-3}$. Positional and thermal parameters are given in Table 1. A list of observed and calculated structure factors is available on request from one of the authors (J. S. R., Jr.).

Table 3

Bond Angles With Estimated Standard Deviations in Parentheses

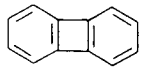
Bond	Angle(°)
C(2a)-N(3)-C(3a)	112.5(1)
N(3)-C(2a)-C(8a)	128.3(1)
N(3)-C(2a)-C(2)	137.6(1)
C(2)-C(2a)-C(8a)	94.1(1)
C(2a)-C(8a)-C(8)	120..1(1)
C(1)-C(8a)-C(2a)	92.3(1)
C(1)-C(8a)-C(8)	147.0(1)
C(7a)-C(8)-C(8a)	114.9(1)
C(8a)-C(8)-H(8)	126.0(9)
C(7a)-C(8)-H(8)	119.0(9)
C(6)-C(7)-C(7a)	120.9(1)
C(6)-C(7)-H(7)	122.4(11)
C(7a)-C(7)-H(7)	116.7(11)
C(5)-C(6)-C(7)	120.4(1)
C(7)-C(6)-H(6)	119.0(11)
C(5)-C(6)-H(6)	120.6(11)
C(4)-C(5)-C(6)	120.5(1)
C(6)-C(5)-H(5)	119.2(11)
C(4)-C(5)-H(5)	120.3(11)
C(3a)-C(4)-C(5)	120.9(1)
C(5)-C(4)-H(4)	119.2(11)
C(3a)-C(4)-H(4)	120.3(11)
N(3)-C(3a)-C(4)	117.8(1)
N(3)-C(3a)-C(7a)	123.6(1)
C(4)-C(3a)-C(7a)	118.6(1)
C(7)-C(7a)-C(8)	121.3(1)
C(3a)-C(7a)-C(8)	119.9(1)
C(3a)-C(7a)-C(7)	118.7(1)
C(1)-C(2)-C(2a)	86.2(1)
C(2a)-C(2)-H(2A)	113.5(9)
C(2a)-C(2)-H(2B)	112.7(9)
C(1)-C(2)-H(2A)	116.1(8)
C(1)-C(2)-H(2B)	114.6(9)
H(2A)-C(2)-H(2B)	111.5(12)
C(2)-C(1)-C(8a)	87.5(1)
C(8a)-C(1)-H(1A)	115.9(9)
C(8a)-C(1)-H(1B)	112.1(8)
C(2)-C(1)-H(1A)	116.2(8)
C(2)-C(1)-H(1B)	115.4(8)
H(1A)-C(1)-H(1B)	109.2(12)

Results and Discussion.

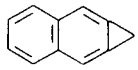
The molecule (Figure 1) is planar and the best least-squares plane including the nitrogen and eleven carbon atoms showed a maximum deviation from planarity of 0.02 Å. A drawing of the molecule is presented in Figure 2 and that of the unit ell in Figure 3. Bond distances and angles with their standard deviations are presented in Tables 2 and 3.

The shortest intermolecular contacts between molecules lying in the same plane are N(3)···C(7) of 3.533 Å, N(3)···H(7) of 2.605 Å, and H(8)···H(2B) of 2.582 Å. The average distance between molecular planes is 3.522 Å These distances are reflective of ordinary Van der Waal's contacts.

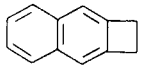
The X-ray structural analysis revealed the accuracy of the earlier calculations. Comparisons of the calculated [1] and observed (present work) carbon-carbon and carbon-nitrogen bond distances and angles show root mean square deviations of 0.020 Å and 1.72°, respectively. The principal effect of the fused small ring is the distortion of the heterocyclic six-membered ring, resulting in a CNC angle of 112.5° (calculated 112.1°). This observed value is less than that for the analogous position in biphenylene (**4**), cyclopropa[*b*]naphthalene (**5**), or any of the cyclobutanaphthalenes (**6-8**) for which structural data have been reported: **4**, 115° [18], **5**, 114.7° [19], **6**, 117.3° [20], **7**, 117.6° [20,21], and **8**, 114.5° [22,23]. Only dicyclobutabenzene **9** is known to have a smaller angle: 108° [24]. A quaternized derivative **10** of 2,7-diazabiphenylene has NCC angles of 114.4° and 119.2° for the analogous positions in the charged and uncharged rings, respectively [25].



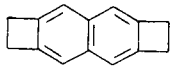
4



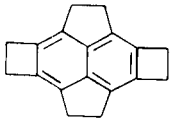
5

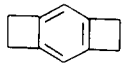


6

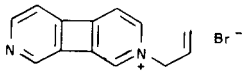


7





9



10

Acknowledgment.

Research at Brookhaven National Laboratory was performed under contract with the U. S. Department of Energy and was supported by its Office of Basic Energy Sciences. Research at Williams College was assisted, in part, by an Innovation Grant from The Camille and Henry Dreyfus Foundation.

REFERENCES AND NOTES

[1] Part 10: D. A. Kleier, W. R. Moomaw, J. H. Markgraf, J. W. Thoman, Jr., and R. N. A. Ridyard, submitted for publication.

[2] Present address: Department of Chemistry, University of Southern Maine, Portland, ME 04103.

[3] J. H. Markgraf and W. L. Scott, *Chem. Commun.*, 296 (1967).

[4] J. H. Markgraf and R. J. Katt, *Tetrahedron Letters*, 6067 (1968).

[5] J. H. Markgraf and R. J. Katt, *J. Org. Chem.*, **37**, 717 (1972).

[6] R. P. Thummel and D. K. Kohli, *J. Heterocyclic Chem.*, **14**, 685 (1977).

[7] R. P. Thummel and D. K. Kohli, *J. Org. Chem.*, **42**, 2742 (1977).

[8] R. P. Thummel and D. K. Kohli, *ibid.*, **43**, 4882 (1978).

[9] R. P. Thummel and D. K. Kohli, *Tetrahedron Letters*, 143 (1979).

[10] A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).

[11] J. H. Markgraf, J. H. Antin, F. J. Walker and R. A. Blatchly, *J. Org. Chem.*, **44**, 3261 (1979).

[12a] T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58**, 1569 (1973); [b] T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., L. D. Brown and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100**, 6595 (1978).

[13] J. H. Markgraf, R. J. Katt, W. L. Scott and R. N. Shefrin, *J. Org. Chem.*, **34**, 4131 (1969).

[14] W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1957).

[15] DIFSYN, a differential synthesis crystal structure refinement program, R. K. McMullan, unpublished (1979).

[16] "International Tables for X-Ray Crystallography", Vol 3, Table 3.3.1 A, Kynoch Press, Birmingham, 1962.

[17] R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[18a] J. K. Fawcett and J. Trotter, *Acta Cryst.*, **20**, 87 (1966); [b] A. Yokozeki, C. F. Wilcox, Jr., and S. H. Bauer, *J. Am. Chem. Soc.*, **96**, 1026 (1974).

[19] W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness and J. L. Wood, *ibid.*, **95**, 7878 (1973).

[20a] J. L. Crawford and R. E. Marsh, *Acta Cryst.*, **B29**, 1238 (1973); [b] T. C. W. Mak and J. Trotter, *ibid.*, **17**, 610 (1964).

[21] J. D. Korp and I. Bernal, *J. Am Chem. Soc.*, **101**, 4273 (1979).

[22] H. Hart, A. Teuerstein, M. Jeffares, W.-J. H. Kung and D. L. Ward, *J. Org. Chem.*, **45**, 3731 (1980).

[23] H. Hart, M. Jeffares, A. Teuerstein and D. L. Ward, *J. Am. Chem. Soc.*, **100**, 8012 (1978).

[24] J. L. Lawrence and S. G. G. MacDonald, *Acta Cryst.*, **B25**, 978 (1969).

[25] S. Kanoktanaporn, J. A. H. MacBride and T. J. King, *J. Chem. Res. (M)*, 2911 (1980).