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X-RAY CRYSTAL STRUCTURE OF DIBENZO[*a,d*]CYCL[2.2.3]AZINES

Kiyoshi Matsumoto,* Hirokazu Iida, Seisuke Mimori, Hiroshi Hamana, Takane Uchida,† and Akikazu Kakehi#

Faculty of Pharmacy, Chiba Institute of Science, Shiomi-cho 15-8, Choshi, Chiba 288-0025, Japan (e-mail: kmatsumoto@cis.ac.jp). †Faculty of Education and Regional Studies, University of Fukui, Fukui 910-8507, Japan, # Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University Nagano 380-8553, Japan

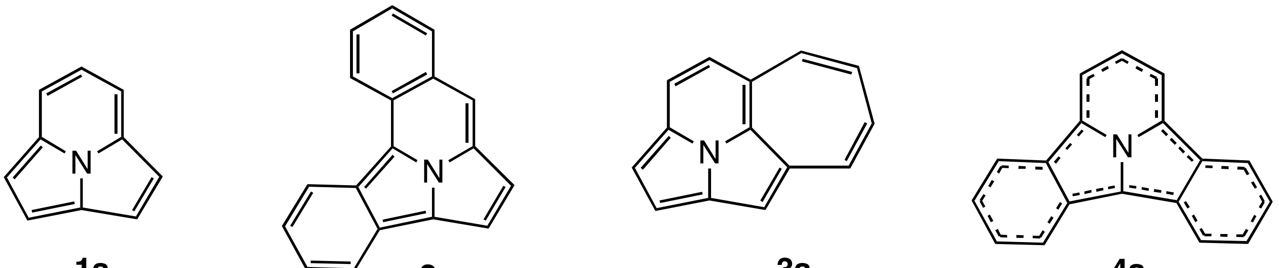
This paper is dedicated to Professor Ekkehard Winterfeld on the occasion of his 75th birthday.

Abstract – The results of X-ray analyses of a novel type of heterocycles, 2-benzoyl- and 1,3-dimethyldibenzo[*a,d*]cycl[2.2.3]azines were described, which offer further evidence for the 18π peripheral conjugate nature of dibenzo-[*a,d*]cycl[2.2.3]azines. The molecules are essentially planer as is the parent cycl[2.2.3]azine, but less strained.

INTRODUCTION

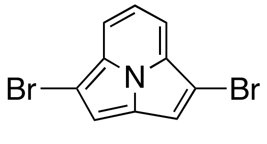
Since Boekelheide *et al.* reported the first synthesis of cycl[2.2.3]azines,[1] the chemistry of cyclazines has attracted much attention in their synthetic and physicochemical aspects.[2] Specifically, peripheral conjugate heterocyclic systems such as bridged heteroannulenes and cyclazines are desired in order to obtain experimental evidence regarding the recognition of the net energy changes associated with π-electron delocalizations. Cycl[2.2.3]azine (**1a**)[3] is a typical example, giving a peripheral 10π electron conjugate system. However, little is known about a π-perimeter system larger than the parent cyclazine (**1**) despite the potential aromaticity of the structure, though dibenzo[*a,h*]cycl[2.2.3]azine (**2**)[4] and the slightly more complex cyloheptadiene-fused cycl[2.2.3]azine system (**3a**)[5] have been known (Scheme 1). We previously reported a facile formation of several substituted dibenzo[*a,d*]cycl[2.2.3]azines (DBCs: **4**).[6] Consecutive studies on **4** by means of ESR,[7] ^{14}N NMR and correlations of oxidation potentials with HOMOs[8] have strongly suggested that the dibenzo[*a,d*]cycl[2.2.3]azine system is considered to be an 18 π perimeter. However, there exist only three examples of X-ray analyses.[5,9,10] As early as 1961 after

Boekelheide succeeded to prepare **1a** in 1959, the crystal structure of 1,4-dibromocycl[2.2.3]azine (**1b**) was reported by Hanson,[9] though the analysis of the parent cycl[2.2.3]azine **1a** failed.[10] The molecule **1a** is almost exactly planar, thus is considered to be 10 π aromatic. The compound (**1a**) forms the 1:1 complex with 1,3,5-trinitrobenzene whose crystal and molecular structure was investigated also by Hanson.[11] We now report the results of X-ray analyses of some of the dibenzo[*a*,*d*]cycl[2.2.3]azines in a preliminary fashion.

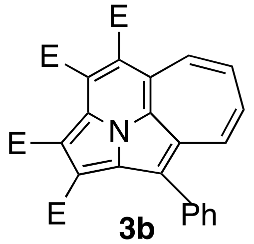


1a **2** **3a** **4a**

Scheme 1. Cycl[2.2.3]azine (**1a**) and their analogs **2**, **3a**, **4a**

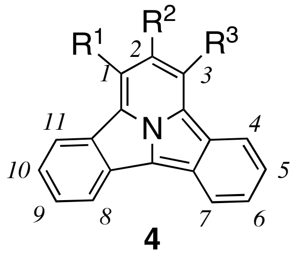


1b



3b

E=CO$_2$Me



4

b: R^1=R^3=H, R^2=Me, **c:** R^1=R^3=H, R^2=Ph,
d: R^1=R^3=H, R^2=PhCO, **e:** R^1=R^3=H, R^2=MeCO$_2$,
f: R^1=R^3=H, R^2=Ac, **g**: R^1=R^2=Me, R^3=H,
h:R^1=R^3=Me, R^2=H

RESULTS AND DISCUSSION

The analysis of **1a** was reported by Hanson to be unsuccessful because of the X-ray data were found to be consistent with free rotation of the molecule in its own plane.[10] Furthermore, the analysis of a dibromo derivative **1b** was of limited accuracy because of difficulties with specimen as well as the disproportionately large scattering power of the Br atoms.[9] After 16 years later, the same author reported the results of the analysis of the 1:1 complex of **1a** with 1,3,5-trinitrobenzene where reversible two phases exist depending on temperature, though the structure of **1a** was essentially same.[11] Below, we describe the results of preliminary comparisons of **1a** with ours.

Firstly, we attempted to perform an X-ray analysis of the unsubstituted one **4a**. The crystals available were orange flakes and were not suitable for an analysis even on repeated recrystallizations. Then, therefore, other substituted **4b-h** were also attempted. Among them, we were able to obtain suitable single crystals of **4d** and **4h** for X-ray analyses. The crystal data are summarized in Table 1. Crystals of **1a**[11] and **4d** are monoclinic, *P2₁/n*, while those of **4h** are triclinic, *P−1*. As expected, **1a** is essentially planer,

Table 1. Summary of crystal data of **4d** and **4h**

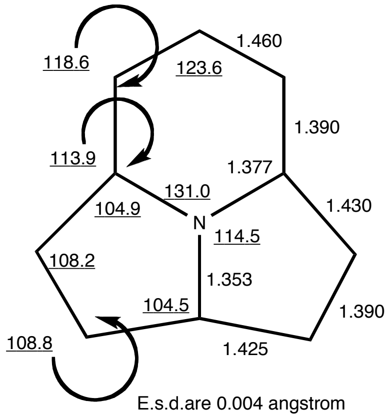
Crystal data	**4d**	**4h**
Formula	$C_{25}H_{15}NO$	$C_{20}H_{15}N$
M (a.m.u.)	345.40	269.38
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (#14)	P1 (#2)
a/ Å	16.57 (1)	12.004 (7)
b/ Å	5.616 (4)	11.992 (6)
c/ Å	20.082 (6)	11.386 (8)
α/ °	------	118.84 (4)
β/°	111.46 (3)	89.25 (6)
γ/°	-------	100.72 (5)
U/ Å^3	1739 (2)	1405 (2)
Z	4	4
*D*c (g cm^{-3})	1.319	1.273
μ (cm^{-1})	0.75	0.69
F (000)	748	568
Radiation (Mo-Kα)		
ν/ Å	0.71069	0.71069
T/°C	24	20
Orienting reflections,.Range	20.1<2θ<26.7	32.5<2θ<37.6
Scan method	ω−2θ	ω−2θ
Data collection range	6.0<2θ< 54.9	6.0<2θ< 60.0
No. of unique data	3691	8173
Total I>3σ (I)	748	2996
No. of parameters	244	500
R	0.095	0.075
*R*w	0.083	0.072

[a] Diffractometer: Rigaku AFC5R.

possessing bond lengths and angles as shown in Figure 1,[11] while the X-ray analysis of **1b** was complicated by the considerable anisotropy of thermal motion of the bromine atoms.[9] An inspection of the torsion or conformation angles[12] revealed that the dibenzocycl[2.2.3]azines **4d** and **4h** are also unsurprisingly virtually planer, with bond lengths and angles as given in Figure 2 and Figure 3.[12]

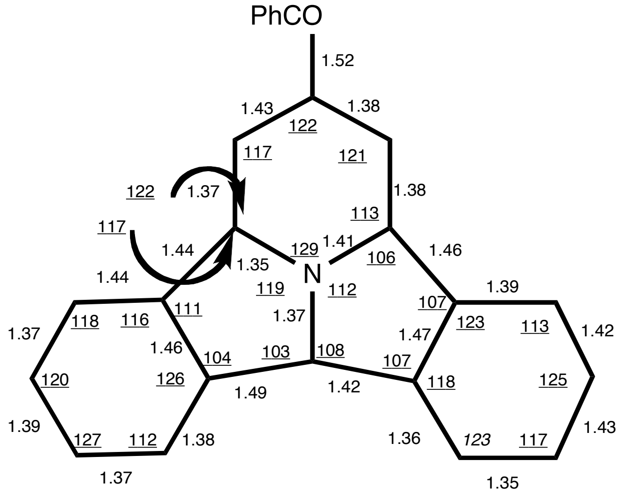
The bond lengths of the pyridine rings of **4d** and **4h** are, except that of C-N bond of **4h**, significantly smaller than those of the parent **1a**, presumably because of higher degree of conjugation due to the fused benzenes. It is also interesting to note that the bond lengths of the non-peripheral pyrrole moieties of **4d** and **4h** are longer than those of **1a**, though one exception (1.35 Å in **4d**) exists. In other words, this fact would offers further evidence for 18π conjugate system of the dibenzocycl[2.2.3]azines.[1]

The apparent symmetry of **1a** is reflected both in NMR[13] and ESR[14] solution studies and in X-ray studies as depicted in Figure 1. This is not the case in the solid sate for **4d** presumably because of the benzoyl



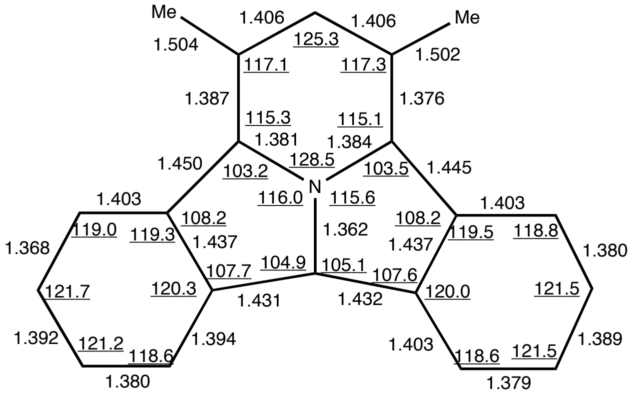
E.s.d.are 0.004 angstrom and 0.3°

Figure 1 Bond lengths (angstrom) and bond angles (°) of **1a**



E.s.d.are 0.02 angstrom and 2°

Figure 2 Bond lenghts (angstrom) and bond angles (°) of **4d**



E.s.d.are 0.005-0.007 angstrom and 0.2-0.5°

Figure 3 Bond lengths (angstrom) and bond angles (°) of **4h** group bent and twisted out of the molecular plane. In solution, **4d** has proved to be symmetric by ^{1}H NMR and ESR studies.[6, 7] Nevertheless the molecular structure of **4h** is intrinsically symmetrical (C2h), there are some discrepancies between chemically equivalent bond lengths and angles such as 4-5 bond vs. 10-11 bond (1.380 vs. 1.368 Å). The compound (**4h**) was found to be C1-symmetry in X-ray analysis due to packing as shown in Figure 3. The similar asymmetry was observed and ascribed to disorder in the solid state.[8,15]

The ^{1}H NMR spectral data of **4d** and **4h** were already reported by us.[6,8] It is interesting to note that, for example, the Me signal of ^{1}H NMR appears at lower field (δ 3.21) than those of benzene derivatives, e.g. toluene (δ 2.35).[16] The Me-C bond lengths of **4h** were 1.504 and 1.502 which seem to be normal for C(sp^3)-C(sp^2) bond.

Analogous trends for molecular symmetry in solid state are apparent by an inspection of bond angles (Figures 1-3). Furthermore, it is evident that **1a** is more strained than **4d** and **4h**. For example, the C-N-C bond angle of the pyridine moiety of **1a** is larger than those of **4d** and **4h** (131 vs. 129 ^{o}).

In conclusion, the results of the X-ray analyses are also in agreement with the previous postulate that the dibenzo[*a,d*]cycl[2.2.3]azine system is an 18π perimeter. Theoretical investigations to reproduce the experimental structures are underway.

Crystal Structure Determination.

Summaries of the crystal data and structure refinement details are given in Tables 1. The structure was solved by a direct method,[17] and refined by full matrix least squares. The atoms other than hydrogen were refined anisotropically. The atomic scattering factors for all atoms and the anomalous dispersion correction factors for atoms other than hydrogen were taken from the literature.[18-20] All calculations were performed using the TEXSAN[21] crystallographic software package of the Molecular Structure Corporation.

ACKNOWLEDGEMENTS

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