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FIRST OBSERVATION OF CATION RADICALS IN THE CYCL[3.2.2]AZINE SYSTEM: 18Π ELECTRON STRUCTURE OF 1,2,3,4-DIBENZOCYCL[3.2.2]AZINES AS REVEALED BY ESR ANALYSIS

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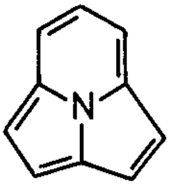
Dedicated to Professor Rolf Huisgen on the occasion of his 65th birthday

Abstract—The cation radicals can be generated by annulation of the dibenzo groups to the cycl[3.2.2]azine system. The use of unpaired electron density as a probe for electronic structure shows (ESR analysis) that the 1,2,3,4-dibenzocycl[3.2.2]azines constitute a novel 18π peripheral conjugate system in spite of large resonance stabilization of benzene nucleus.

Peripheral conjugate heterocyclic systems such as bridged heteroannulenes and cyclazines are desired in order to obtain experimental evidence regarding our recognition of the net energy changes associated with π-electron delocalizations.[1] Specifically, the unpaired electron distribution of an anion radical species from cycl[3.2.2]azine (1) has been clarified by an ESR spectroscopy, offering validity to a π-electron approximation for this type of compounds.[2,3] However, neither cation radical formation from cycl[3.2.2]azines and therefore nor their ESR study has been reported; this suggests considerable stability of this 10π-peripheral system.[4]

This communication reports preliminary results on the first observation of cation radicals from the cycl[3.2.2]azine system in which two benzene nucleus are annulated at 1,2,3,4 positions, e.g. 1,2,3,4-dibenzocycl[3.2.2]azines (2).[5,6] In contrast to 1, cation radical species can be readily generated from 2a upon oxidation with



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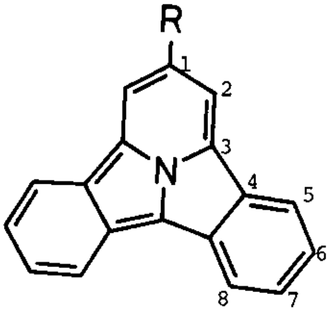

2a, R=H

2b, R=PhCO

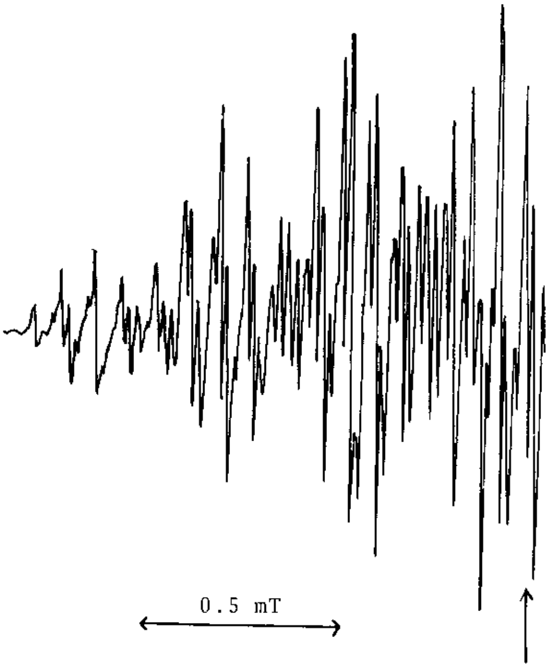

Fig. 1. ESR spectrum of the cation radical of 2a

$AgClO_4$, though attempts to form stable anion radical species were unsuccessful. 6-Benzoyl-1,2,3,4-dibenzocycl[3.2.2]azine (2b) gave both radical species through the conventional oxidation and reduction methods. These facts reflect a strong effect of the annulation of the dibenzo-groups to the 10π-peripheral conjugate system. Fig. 1 shows a well-resolved ESR spectrum of the cation radical produced from 2a by oxidation with $AgClO_4$ in CH_2Cl_2 at room temperature. From the non-overlapping spectral region, several reliable values of proton hyperfine coupling constants were determined, e.g. two large proton coupling constants, 0.334 and o.318 mT come from two groups of the two equivalent protons attached to the dibenzo-groups. According to MacConnel relation between ESR coupling constants and unpaired electron density, these coupling constants strongly suggest a large amount of unpaired electron density on the dibenzo-peripheral system. An inspection of the ESR spectra of 2a and 2b shows that the proton at the position 1[7] has also a large hyperfine coupling constants (ca. 0.4 mT), whereas almost negligible hyperfine coupling constants of the nitrogen atom were observed in both ESR spectra of 2a and 2b. These results clearly indicate a virtual delocalization of the unpaired electron over the 18π peripheral conjugate system and in other words a large perturbation by extending the peripheral conjugate system from 10π to 18π. These coupling constants simulated by computer were compared with the predicted unpaired electron density calculated from the Hückel MO method where the same integral parameters as were used for 1[2,3] were employed (Table 1). The unpaired electron distributes greatly to the peripheral conjugate system, especially on the dibenzo-groups. The experimental values are found to be slightly greater than the calculated ones.

The HOMO and LUMO energy levels are also influenced by extending the conjugate system. Fig. 2 shows a comparison of these two energy levels of 1 and 2a. Both HOMO and LUMO energy levels of 2a shift upward as compared to those of 1. This shift is in qualitative agreement with easier oxidation and harder reduction of 2a than 1. Indeed, 2a is readily oxidized and hardly reduced under conventional conditions, while 1 is easily reduced but has been unsuccessful to yield cation radicals. 2b, which has an electron-withdrawing group at the position 1[7] can form an anion radical species by alkali metal reduction.[8] This implies that the HOMO and LUMO energy levels lie at the suitable positions so that both oxidation and reduction are allowed.

Table 1. Hyperfine Coupling Constants for the Cation Radicals 2a (and 2b)

Coupling const.[a] [mT]	Calcd. coupling const.[b] [mT]	Assignment Positions[c]
0.415 (-----)	0.217	1
0.334 (0.309)	0.263	8
0.318 (0.288)	0.206	6
0.268 (0.232)	0.108	5
0.087 (0.077)	0.067	7
0.069 (0.069)	0.029	2
0.0 (0.018)	0.031	N

[a] Values obtained by computer simulation of the spectrum. In parentheses values for 2b. [b] Obtained by McConnell equation, $\alpha_H=Q_H\rho$, where $Q_H=2.8$ mT. For HMO parameters, see ref. 2 and 3. [c] Numbering is as depicted in 2. Some of these assignments are only tentative. Confirmation employing specifically deuterium labeled 2a is envisaged.

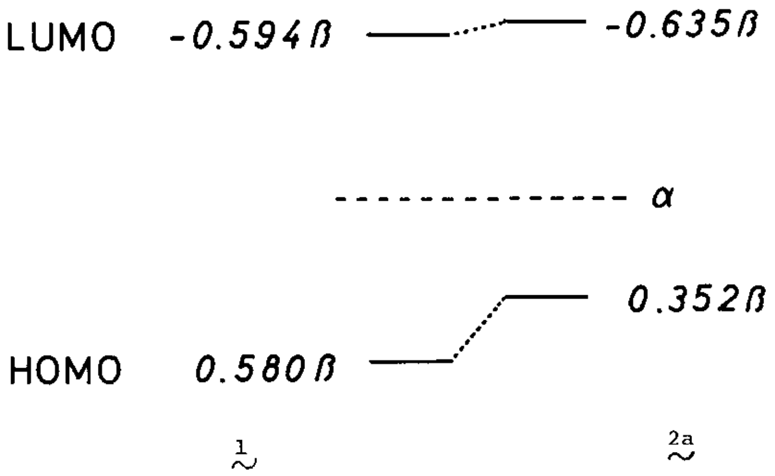

Fig. 2. HOMO and LUMO levels of 1 and 2a

In conclusion, the characteristic behavior of **2** is apparently due to the large (18π) peripheral conjugate systems, e.g., due to the significant perturbation by the dibenzo-groups.

REFERENCES AND NOTES

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2. N. M. Atherton, F. Gerson, and J. N. Murrel, *Mol. Phys.*, 1963, **6**, 265.
3. F. Gerson and J. D. W. van Voorst, *Helv. Chim. Acta*, 1963, **46**, 2257. See also: F. Gerson, J. Jachimowicz, and D. Leaver, *Helv. Chim. Acta*, 1973, **56**, 258.
4. In contrast to **1**, both cation and anion radicals were produced from cycl[3.3.3]-azine, a 12π perimeter, by usual methods. The ESR analysis indicated that the peripheral conjugate system has non-bonding HOMO and anti-bonding LUMO. These two MOs correspond well with SOMOs of the cation and anion radicals. Thus, the HOMO and LUMO of cycl[3.3.3]azine lying near non-bonding energy level enabled the observation of both radical species: F. Gerson, J. Jachimowicz, and D. Leaver, *J. Am. Chem. Soc.*, 1973, **95**, 6702.
5. According to IUPAC nomenclature, this may be named benzo[a]isoindolo[1,2,3-cd]-indolizine. In this paper we use the Boekelheide nomenclature.[1]
6. **2a-b** were prepared by 1,3-dipolar cycloaddition of pyridinium dicyanomethylids with benzyne: K. Matsumoto, T. Uchida, T. Sugi, and Y. Yagi, *Chem. Lett.*, 1982, 869. Review on heterocyclic mesomeric betains: W. D. Ollis, *Tetrahedron*, 1985, **41**, 2239.
7. For convenience, numbering is as depicted in formula **2**.
8. Full details regarding this and others' aspects will be reported in a full paper.

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