Polish J. Chem., **76**, 1249–1254 (2002)

Angular Group Induced Bond Alternation (AGIBA). Part VIII. Crystal and Molecular Structure of 2,3,6,7-Tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde(E,E)-azine. A Competition Between the AGIBA and the Through Resonance Effects*

by T.M. Krygowski, E. Pindelska, R. Anulewicz-Ostrowska and J. Nowacki

Department of Chemistry, University of Warsaw, 02-093 Warsaw, Pasteura 1, Poland

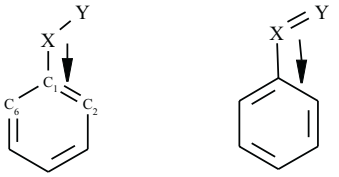
(Received January 30th, 2002; revised manuscript February 27th, 2002)

Low temperature (100 K) X-ray diffraction study of 2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde(E,E)-azine provided the molecular geometry allowing to study a competition between the AGIBA and through resonance effects. The simplified derivatives, for which geometry was obtained by optimization at B3LYP/6-311G** level of theory, supported the results for the title compound and the conclusion that the AGIBA effect and the through resonance may exist simultaneously in systems with appropriate substituents.

Key words: *ab-initio* calculations, substituent effects, AGIBA effect

Angular groups attached to the mono- and poly-cyclic π electron systems cause substantial changes in the structural parameters [1–4], known as Angular Group Induced Bond Alternation (AGIBA) [5–7]. These effects are schematically presented by Scheme 1: the single and double bonded groups cause shortening and lengthening of the *cis* – CC bond in benzene ring, respectively.

Scheme 1



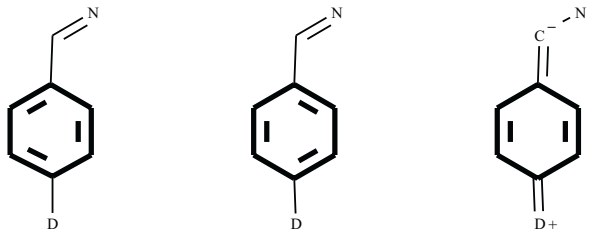
The local structural changes are typical for polycyclic systems [7], whereas in monocyclic systems are propagated over the whole aromatic rings like benzene or *s*-triazine [3] and even non- or weakly-aromatic like borazine and boroxine [8]. The

*Presented at the 1st Russian-Ukrainian-Polish Conference on Molecular Interactions in Gdańsk, June 2001, (Poland).

effect is strongly conformation dependent [1,7] and additive when the angular groups are attached to the ring [9]. However, if the angular group forms a branched substituent (like *e.g.* the carboxyl group), the effect does not appear at all [10].

However, in some cases π-electron ring may be substituted by various groups, which exhibit also a usual electronic effect like a resonance one, which might compete with the AGIBA effect, if the substituents are in *para* position and of the opposite electronic nature [11,12]. A typical representation of the latter kinds of interactions may be given by canonical structures K1, K2 and Q, as shown in Scheme 2:

Scheme 2



K1 K2 Q

where D denotes the electron – donating substituent. Canonical structures K1 and K2 represent the situation, in which there is no resonance effect of the substituents, whereas the canonical structure Q describes the through resonance effect between the electron – donating and electron – accepting groups, respectively. The 2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde(E,E)-azine, labelled throughout the paper as **1,** is a case in which one can expect some through resonance effect between the amino- and the –C=N groups, which may be in coincidence with the AGIBA effect.

The aim of this paper is to analyse how these two kinds of effects interfere in the title system. To make situation free from intermolecular interactions, the optimized geometry of a few simplified model systems was computed by use of B3LYP/6-311G** [13].

EXPERIMENTAL

Preparation: Synthesis of **1**: To the vigorously stirred mixture of 0.2 g. (1.0 mmole) of aldehyde and 0.025 ml (0.5 mmole) of 80% hydrazine hydrate, 2 ml of methanol was added. The orange solid product, which precipitated instantly, was filtered off and recrystallized from methanol – methylene chloride mixture giving pure azine, m.p. > 360°. Yield: 0.17 g (85%).

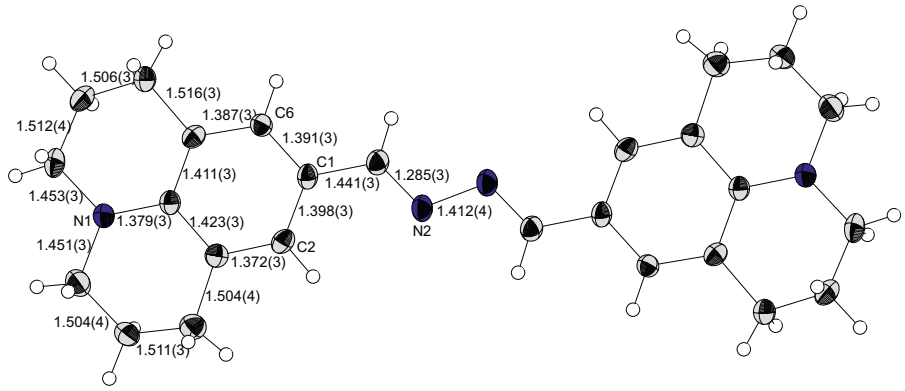
Crystal structure determination: Crystal data regarding the structure of **1** are given in Table 1, together with refinement details. All measurements of the crystals were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. The crystal was positioned at 62 mm from the KM4CCD camera. 496 frames were measured at 1.5° intervals with a counting time of 25 sec. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs. The struc-

ture was solved by direct methods [14] and refined using SHELXL [15]. The refinement was based on F^2 for all reflections, except those with very negative F^2. The weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_0^2 > 2s(F_0^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in [16]. Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 178452. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int code + 44 (1223)336-033; E-mail:deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement of 2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde(E,E)-azine in temperature 100 K.

Empirical formula	$C_{26}H_{30}N_4$
Formula weight	398.54
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P*2(1)/*c*
Unit cell dimensions:	*a* = 7.971(2) Å
	b = 8.030(2) Å
	c = 16.541(3) Å
	β = 93.62(3)°
Volume	V = 1056.6(4) Å^3
Z	2
Calculated density	1.253 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	428
Crystal size	0.45 × 0.4 × 0.3 mm
Theta range for data collection	3.44 to 22.50 °
Index ranges	–10 <= h <= 10
	–10 <= k <= 10
	–21 <= l <= 22
Reflections collected/unique	12112/1376
	R(int) = 0.0518
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1376/0/137
Goodness-of-fit on F^2	1.105
Final *R* indices [*I* > 2sigma(*I*)]	*R*1 = 0.0741
	wR^2 = 0.2010
R indices (all data)	*R*1 = 0.0880
	wR^2 = 0.2204
Extinction coefficient	0.000(5)
Largest diff. peak and hole	0.490 and –0.285 e Å^{-3}

Scheme 3

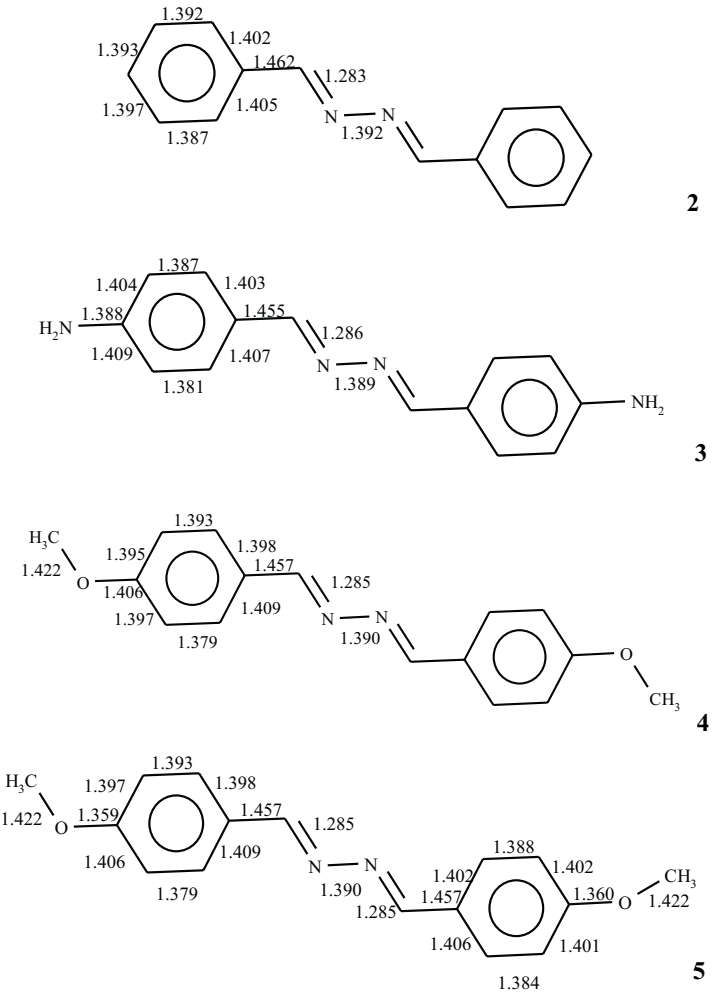


RESULTS AND DISCUSSION

Experimental geometry: Experimental geometry of **1** (Scheme 3) shows that the local AGIBA effect is well defined: the difference between C_1C_2 and C_1C_6 is 0.007 Å. Taking into account the whole ring, its geometry allowed to estimate the canonical structure weights by use of HOSE model [17], leading to the imbalances of K1 and K2 as 35.8:24.9. This means a quite substantial AGIBA effect. The through resonance is slightly stronger, at least considering a value of Q that is 39.3%. In molecules of compound **1** there are also present some strain effects, which may give rise to effects which may obscure the picture. For these reasons we have also undertaken the optimization (B3LYP/6-311G**) [13] of systems, which might be good models for a direct study of the interplay between the AGIBA and through resonance effects. In the case of the monosubstituted ring of **2** (Scheme 4), the AGIBA effect appears rather weak with the imbalance K1:K2 = 35.4:31.0 and with the Q – weight equal to 33.6%. If we take the difference $\Delta = K1 - K2$ as a measure of power of the AGIBA effect, for this case $\Delta = 4.4\%$. In the case of the *para*-amino derivative, **3** of Scheme 4, the imbalance changes to the ratio 33.1:28.0 with Q = 38.9%. We observe a decrease of both K1 and K2, due to a strong through resonance effect implying an increase of Q. But it is worth mentioning the difference $\Delta = K1 - K2$ increases in this case to the value $\Delta = 5.1\%$.

Detailed inspection in geometry of two conformers (**4** and **5**) shows dramatic differences. In the first case (**4**), when both methoxy groups work in line with C=N group, the canonical structure ratio is K1:K2:Q = 37.7:27.9:34.4 indicating a substantial AGIBA effect born from the action of both substituents. In another case (**5**), one methoxy group is forced to be in the anti-AGIBA conformation. The difference between molecular geometry of two rings in this case is very large. The ring, in which both substituents work in line, has the canonical structure ratio similar to the former case: K1:K2:Q = 38.3:26.1:35.6. A dramatic difference is observed for another ring, where the substituents work one against another. The canonical structure ratio is K1:K2:Q = 33.0:30.5:36.5. Note that in all three cases Q is almost the same, about

35–36%, whereas the imbalance K1:K2 changes dramatically from about 27:37 to 33:30. It means, that through resonance effect working in all three cases is practically independent of the AGIBA effect, which in turn is strongly conformation dependent.



Scheme 4. Molecular geometry of model compounds [B3LYP/6-311G** optimization].

CONCLUSIONS

The AGIBA effects, despite of their low energetical consequences [18] are observed in cases when the competition with the through resonance is present. A low imbalance of the Kekule structures in **1** may be the result of a strain in the title system.

Acknowledgments

E. P. acknowledges the Interdisciplinary Centre for Mathematical and Computational Modelling (Warsaw University) for computational facilities. The Polish State Committee for Scientific Research (3T09A 114 18 grant) provided financial support for this study. The X-ray measurement was undertaken in the Crystallographic Unit of the Physical Chemistry Lab. at the Chemistry Department of the University of Warsaw. Authors wish to thank the referee for showing us some inconsistences in our experimental work.

REFERENCES

1. Krygowski T.M., Anulewicz R., Jarmuła A., Bąk T., Rasała D. and Howard S.T., *Tetrahedron*, **50**, 13155 (1994).
2. Howard S.T., Krygowski T.M. and Główka M.L., *Tetrahedron,* **52**, 11379 (1996).
3. Krygowski T.M., Howard S.T., Martynowski D. and Główka M.L., *J. Phys. Org. Chem*, **10**, 125 (1997).
4. Krygowski T.M., Anulewicz R. and Hiberty P.C., *J. Org. Chem.,* **61**, 8533 (1996).
5. Krygowski T.M., Wisiorowski M., Howard S.T. and Stolarczyk L.Z., *Tetrahedron*, **53**, 13027 (1997).
6. Howard S.T., Krygowski T.M., Ciesielski A. and Wisiorowski M., *Tetrahedron*, **54**, 3533 (1998).
7. Krygowski T.M., Pindelska E., Cyrański M.K. and Grabowski S.J., *Tetrahedron*, **56**, 8715 (2000).
8. Maulitz A.H., Stellberg P. and Boese R., *J. Mol. Struct*., **338**, 131 (1995).
9. Krygowski T.M., Pindelska E., Anulewicz-Ostrowska R., Grabowski S.J. and Dubis A., *J. Phys. Org. Chem.,* **14**, 349 (2001).
10. Krygowski T.M. and Pindelska E*., Polish J. Chem*., **76**, 325 (2002).
11. Krygowski T.M., Piętka E., Anulewicz R., Cyrański M.K. and Nowacki J., *Tetrahedron*, **54**, 12289 (1998).
12. Pindelska E., Krygowski T.M., Anulewicz-Ostrowska R., Cyrański M.K. and Nowacki J., *J. Phys. Org. Chem.*, **14**, 764 (2001).
13. Frisch M.J., Trucks G.W., Schlegel H.B., Gill P.M.W., Johnson B.G., Robb M.A., Cheesman J.R., Keith T., Peterson G.A., Montgomery J.A., Raghavachari K., Al-Laham M.A., Zakrzewski V.G., Ortiz J.V., Foresman J.B., Cioslowski J., Stefanov B.B., Nanayakkara A., Challacombe M., Peng C.Y., Ayala P.Y., Chen W., Wong M.W., Andres J.L., Replogle E.S., Gomperts R., Martin R.L., Fox D.J., Binkley J.S., Defrees D.J., Baker J., Stewart J.P., Head-Gordon M., Gonzales C. and Pople J.A., *Gaussian 94*; Gaussian Inc. Pittsburgh PA, 1995.
14. Sheldrick G.M., *Acta Cryst*., **A46**, 467 (1990).
15. Sheldrick G.M., SHELXL93. *Program for the Refinement of Crystal Structures,* Univ. of Göttingen, Germany.
16. *International Tables for Crystallography*, Ed. A.J.C. Wilson, Kluwer: Dordrecht, Vol. C.**15** (1992).
17. Krygowski T.M., Anulewicz R. and Kruszewski J., *Acta Cryst.,* **B39**, 732 (1983).
18. Krygowski T.M., Cyrański M. and Wisiorowski M., *Polish J. Chem*., **70**, 1351 (1996).