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Separation of the Energetic and Geometric Contributions to the Aromaticity. Part IV. A General Model for the π-Electron Systems.

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Abstract. Application of the Pauling bond number[1] to the aromaticity index HOMA[2-3] allowed us to extend its separation into the geometric and energetic contributions for the hetero π-electron systems. The energetic term (EN) represents the part related to resonance energy of a given system. The geometric term represents dearomatization due to an increase of bond length alternation (localisation of double bonds). The Bird indices I_5 and I_6[4] well represent aromatic character due to its geometric features. In most cases geometric contributions play a significant role and variation in GEO-term is the most important factor in variation of HOMA values and their correlation with Bird's indices. Aromaticity indices for 24 five- and six -membered, most typical, heterocyclic systems are presented and discussed. Copyright © 1996 Published by Elsevier Science Ltd

Introduction

Aromaticity is one of the most fundamental concepts of organic chemistry.[5-7] In the last decade it has been deduced that it is a multidimensional phenomenon.[8-11] Application of the principal component[12] or factor analyses[12] to the large data matrices composed of many various aromaticity indices for hetero- or carbocyclic π-electron systems have shown that two[9] or even three[8] independent factors are necessary to describe about 80% of the total variance. These studies are opposed by another idea that the (calculated) magnetic properties of π-systems are the most representative ones for the phenomenon of aromaticity.[13-15] Recently it has also been shown that local aromaticity may depend strongly on the nature of the topological[10,16] and chemical[3,10,17] environment. The aromaticity index HOMA[2-3] of the phenylic ring in p-nitroso phenolate anion in various crystalline salts depended strongly on the net of H-bonding water molecule.[3] The same index for benzene rings embedded in various topological environments in benzenoid hydrocarbons varied from 0 till 0.99 indicating a considerable change in aromatic character.[10] Recently Katritzky et al.[18] have shown that the aromatic character of most heterocycles and some carbocycles increases with polarity of the medium. It has also been found[19] that the aromatic character of the ring in exocyclically substituted derivatives of benzylic cations considerable decreases with an increase of delocalization of the positive charge of the ring. In view of the above it seems valuable to develop the method enabling the study of local aromatic character of molecules.

The aromatic character of various carbo- and heterocyclic π-electron systems has been widely studied by the HOMA index (eq.1).[2-3, 20-25]

$$HOMA = 1 - \frac{\alpha}{N}\sum\left[R_{opt} - R_i\right]^2 \qquad (1)$$

where N is the number of bonds taken into summation and α is an empirical constant fixed in a way to get HOMA = 0 for the Kekule structure of the typical aromatic system, and equal to 1 for the system with all bonds equal to the optimal value R_{opt}. Its high utility is mostly due to the fact that it applies experimentally derived bond lengths.

Very recently, it has been shown for carbocyclics that the index of aromaticity HOMA[2-3] (eq. 1) may be analytically[26] divided into two terms describing the energetic EN and geometric GEO contributions to the overall index of aromaticity (eq.2).

$$HOMA = 1 - \alpha\left(R_{opt} - R_{av}\right)^2 - \frac{\alpha}{N}\sum\left(R_{av} - R_i\right)^2 = 1 - EN - GEO \qquad (2)$$

The EN and GEO terms, may be interpreted as the dearomatization terms describing a decrease of aromaticity due to a decrease of the resonance energy, and an increase of bond length alternation, respectively. It is important to say that EN and GEO terms are not correlated with each other. Application of equation (2) to estimate the local aromatic character of the individual benzene ring embedded in different topological environments revealed several interesting features: (i) the aromatic character depends strongly on the topology of the closest environment, and (ii) dearomatization may be due to either EN or GEO - or both those terms.[16] When equation (2) was applied to differently substituted benzene derivatives, variation of the aromatic character of the ring was found to be much smaller.[17]

The most thorough studies on the aromatic character of various heterocyclic systems have been published in the last decade by Bird.[4] The indices I_5 and I_6 are proportional to the variance of bond lengths transformed into the bond orders by using the Gordy formula,[27] so they describe the geometric contribution to the aromaticity.[26]

The aim of this paper is to extend the model, based on the idea of HOMA index, however, such that will enable separation of aromaticity into the energetic and geometric contributions for the heterocyclic π-electron systems.

The model

Equation (2) shows how the aromaticity may be separated into the energetic and geometric contributions for the carbocyclic π-electron systems only. Unfortunately, averaging of bond lengths cannot be carried out for bonds with heteroatoms. This problem was originally solved by introducing the concept of optimal bond length in the HOMA model,[2] or by Bird[4] by use of the Gordy[27] relation between the bond length and bond order. The Bird indices I_5 and I_6 are based principally on the value of variance calculated from the bond orders of the ring in question, and hence they represent the aromatic character due to the geometric term, i.e. variance in alternation of bond lengths. The advantage of the HOMA index is that it contains both the energetic and geometric

contributions,[26] as shown in eq. (2). Therefore we have applied the Pauling concept of bond number[1] for extension of the HOMA model, including its most recent modifications[26] for the systems with heteroatoms.

The Pauling idea consist in the postulated relation between the bond length R(n) and its bond number n:[1]

$$R(n) - R(1) = -c\ln(n) \qquad (3)$$

This concept has been successfully applied to many chemical problems[10-11, 28-31] and it therefore seems reasonable to use it for extension of the HOMA model in a version which separates the energetic and geometric contributions. From eq (2) it is clear that taking bond lengths for the typical single, R(1), and double , R(2), bonds with bond number n = 1 and 2, respectively, one can estimate the value of constant c.

$$c = \exp\frac{R(1) - R(2)}{\ln 2} \qquad (4)$$

This is a characteristic feature of the given kind of bonding. From eq (3) it is also possible to calculate the bond number, n, for any bond length, R(n).

$$n = \exp\frac{R(1) - R(n)}{c} \qquad (5)$$

Using the optimal bond lengths R_{opt}[3] in eq. 4 one obtains the "optimal bond number", n_{opt}, the fundamental parameter in this extended HOMA model:

$$n_{opt} = \exp\frac{R(1) - R_{opt}}{c} \qquad (5a)$$

All these empirical parameters, such as c or n_{opt} are calculated from the most precise reference bond lengths available, taken from reference.[3] Table 1 summarises all the relevant data; (R(1), R(2), R_{opt} and c are in Å, n_{opt} is dimensionless).

Table 1. Structural parameters of HOMA index for heterocyclics.

	R(1)	R(2)	R_{opt}	c	n_{opt}
CC	1.467	1.349	1.388	0.1702	1.590
CN	1.465	1.269	1.334	0.2828	1.589
CO	1.367	1.217	1.265	0.2164	1.602
CP	1.814	1.640	1.698	0.2510	1.587
CS	1.807	1.611	1.677	0.2828	1.584
NN	1.420	1.254	1.309	0.2395	1.590
NO	1.415	1.164	1.248	0.3621	1.586

As could be intuitively expected, n_{opt} has practically the same value for all bonds in question, i.e. in the range between 1.584 and 1.602. Therefore we take n_{opt}= 1.590 for all bonds in question.

Now, replacing bond lengths R_i by the respective bond numbers n_i in eq. (1) we obtain the formula for HOMA with separation into the energetic and geometric terms for hetero-π-systems *but expressed in terms of bond numbers*:

$$HOMA = 1 - \frac{\alpha}{N}\Sigma\left(n_{opt} - n_i\right)^2 = 1 - \left[\alpha\left(n_{opt} - n_{av}\right)^2 + \frac{\alpha}{N}\Sigma\left(n_{av} - n_i\right)^2\right] \qquad (6)$$

where N in the number of bonds taken into calculation. The α-value may be obtained from the normalisation condition, that HOMA = 0 for the Kekule structure with alternated single and double bonds (of the lengths as reported in Table 1)

$$1 = \frac{\alpha}{6}3\left[\left(1.590 - 1\right)^2 + \left(1.590 - 2\right)^2\right] \Rightarrow \alpha = 3.874$$

The problem however arises, that the quantities building up the squared differences in (6) *are not linear in bond lengths, but they are rather their exponential functions.* Therefore the HOMA values estimated for carbocyclics by use of formula (6) differ significantly from those obtained by the original formula (1). Table 2 presents the statistical parameters describing linear regressions between the data obtained by use of formulas (1) and (6).

Table 2. Statistical parameters describing the dependence of HOMA-values (eq. 6) on the original values of HOMA (eq. 1). I and S. stand for the intercept and slope, respectively; C denotes the correlation coefficient.

	Sample size	H(1) / H(6)		Sample size	H(1) / H(6)
Benzene rings in benzenoid hydrocarbons	169	I= 0.020 S= 0.930 C= 0.964	TCNQ-EDA-complexes and salts	90	I= -0.165 S= 1.169 C= 0.980
cyclopentadienyl rings in complexes with Rh	48	I= 0.0324 S= 0.948 C= 0.984	benzene ring in substituted nitrobenzene derivatives	184	I= -0.330 S= 1.33 C= 0.995
Nitrogen containing rings in aza-benzenoid hydrocarbons	47	I= 0.078 S= 0.876 C= 0.983	Metalorganic complexes of phosphole	25	I= 1.0058 S= 0.900 C= 0.997
Organic derivatives of thiophene	83	I= -0.267 S= 1.247 C= 0.946	Organic derivatives of tetrazole	30	I= -0.209 S= 1.218 C= 0.993
Organic derivatives of furane	113	I= -0.098 S= 1.309 C= 0.876			

In most cases there is a very good correlation, i.e. correlation coefficients (C) close to 1.0, but the regression coefficients (S) differ considerably from 1.0. These discrepancies are the result of the above-mentioned mathematical difference between eqs (1) and (6). In order to diminish these discrepancies we have further modified eq (6) in which we have transformed bond numbers, n, for CX bonds, or generally XY bonds, into the virtual CC bond lengths by use of formula (3) presented in a detailed form:

$$r(n) = 1.467 - 0.1702 \ln(n) \qquad (7)$$

These bond lengths are denoted in further text and formulas by r, in opposition to R denoting the original bond lengths. Note that the R_{opt} is not changed, it is the value for CC bonds. The bond lengths calculated by formula (7) from the bond numbers for XY bonds are then used in the general formula for HOMA:

$$HOMA = 1 - \left[257.7 \left(1.388 - r_{av}\right)^2 + \frac{257.7}{N} \Sigma \left(r_{av} - r_i\right)^2 \right] \qquad (8)$$

with parameters of the model r_{opt} = 1.388 Å and α= 257.7 Å^{-2}

Based on the reasoning presented in detail in ref.[26] the formulas for the GEO, EN and HOMA terms are as follows:

$$HOMA = 1 - EN - GEO \qquad (9)$$

where

$$EN = \alpha \left(r_{opt} - r_{av}\right)^2 \qquad \text{for } r_{av} > r_{opt} \qquad (9a)$$

and

$$EN = -\alpha \left(r_{opt} - r_{av}\right)^2 \qquad \text{for } r_{av} < r_{opt} \qquad (9b)$$

$$GEO = \frac{\alpha}{N} \sum \left(r_{av} - r_i\right)^2 \qquad (9c)$$

When the above model is applied to heterocyclics, all discrepancies in Table 2 become insignificant since the correlation coefficients for all five linear regressions are always greater then 0.99. Moreover slopes are equal to 1 within the range less than 0.5%. For carbocyclics the results are exactly the same as by using eq. (1) by definition.

Because of the differences on mathematical bases for EN in eq. (6) and in the final formula eq. (9) it was necessary to check up the hypothesis that in both cases the energetic terms are quantitatively equivalent. The high values of correlation coefficients for the relations between EN (eq.6) and EN (eq. 9) C > 0.92 support the hypothesis. In consequence it is also possible to accept the independence of the EN and GEO terms, that was mentioned earlier.

The EN and GEO terms obtained for a series of compounds presented in Table 2 were plotted against the Bird indices: I_6 or I_5. Only the GEO term exhibited good linear dependence with a high and statistically

significant correlation coefficient, supporting nicely our earlier conclusion that Bird's indices describe mostly the geometric contribution to the aromatic character. Additionally, in view of the correlation analysis the EN and GEO terms were found to be linearly independent variables.

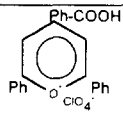
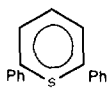
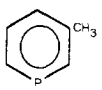
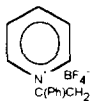
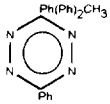
The above-presented model will be applied to numerous groups of hetero-π-systems elsewhere, in the later papers.[32] A few examples for most typical cases are given below.

Illustrative applications

Charts I-II presents HOMA, EN, GEO and Birds I_6 or I_5 indices for a few most popular heteroaromatic, monocyclic compounds with various heteroatoms, which are listed now for illustration of the applicability of the model. In most cases numeric data were available for the substituted species. We have usually selected compounds with weakly interacting substituents.

Chart I presents HOMA, EN, GEO and Birds I_6 for the six-membered heterocyclic system. Only the molecular geometries obtained with the highest precision of the X-ray or neutron diffraction measurements (As=1 and sometimes AS=2,[44]) were taken into account, and the precision of the data is indicated in each figure.

Chart I. Aromaticity parameters for 6-membered heterocycles.

No.	Compound	AS	HOMA (eq. 9)	I_6	No.	Compound	AS	HOMA (eq. 9)	I_6
1[21]		1	H= 0.582 E= 0.101 G= 0.327	53.4	7[38]		1	H= 0.999 E= 0.000 G= 0.001	84.0
2[33]		1	H= 0.829 E= 0.037 G= 0.134	63.7	8[39]		1	H= 1.000 E= 0.000 G= 0.000	86.2
3[34]		1	H= 0.924 E= 0.037 G= 0.039	73.1	9[40]		1	H= 0.982 E= 0.005 G= 0.012	78.8
4[35]		1	H= 0.998* E= -0.009 G= 0.011	81.2	10[41]		1	H= 0.791 E= 0.022 G= 0.187	69.8
5[36]		2	H= 0.973 E= -0.025 G= 0.052	72.3	11[42]		1	H= 1.029 E= -0.029 G= 0.000	100
6[37]		1	H= 0.955 E= 0.001 G= 0.044	78.2	12[43]		2	H= 0.962 E= 0.008 G= 0.030	84.4

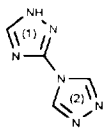
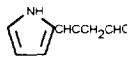
* Mean value of 4 geometries.

Interestingly, all aza-derivatives of benzene exhibit a very high aromatic character with an increase of aromaticity for the cases where nitrogen atoms are separated by carbon atoms. Apart from pyridine (4), the most aromatic ones are pyrimidine (7), pyrazine (8) and s-triazine (11). The most important term in their

dearomatization stems from the alternation of bond lengths (i.e. GEO-term). EN is almost always meaningless. The ring in pyridinium salt (5) loses its aromaticity to a very small extent only due to the charging of the ring. The dearomatization effect here is due to the geometric term; the energetic term acts in the opposite direction. Among three other representatives of six-membered heterocycles the most aromatic one is the phosphine derivative (3), followed by thiopyran (2) and the least aromatic one is pyrylium ring (1). In the last two cases dearomatization is due to the geometric term, but for the pyrylium ring the energetic term is also important.

Chart II presents HOMA, EN, GEO and I_5 for five-membered heterocycles. The most aromatic are the derivatives of pyrrole (16) and thiophene (14) and far away from them the phosphole (15) and furan (13) derivatives. Again the most dearomatising term is due to the bond length alternation, i.e. the GEO term but the energetic term plays a more significant role than in the case of 6-membered heterocycles. In the case of polyaza derivatives, the increasing number of nitrogen atoms in the ring does not change its aromatic character significantly. Dearomatization is mostly due to the geometric term.

Chart II. Aromatic parameters for five-membered heterocycles

No.	Compound	AS	HOMA (eq. 9)	I_5	No.	Compound	AS	HOMA (eq. 9)	I_5
13[45]		1,2*	H=0.029 E=0.108 G=0.863	32.8	19[51]		2	H=0.839 E=0.001 G=0.160	64.1
14[46]		1	H=0.654 E=0.113 G=0.233	67.9	20[52]		1	H=0.911 E=0.027 G=0.062	82.0
15[47]		2	H=0.346 E=0.065 G=0.588	37.0	21[53]		1	(1) H=0.907 E=0.003 G=0.090 (2) H=0.753 E=0.019 G=0.228	(1) 79.0 (2) 63.3
16[48]		2	H=0.899 E=0.004 G=0.097	65.4	22[54]		1**	H=0.885 E=0.015 G=0.100	78.1
17[49]		1	H=0.922 E=0.019 G=0.059	75.9	23[55]		1	H=0.973 E=0.001 G=0.026	88.3
18[50]		1	H=0.918 E=0.007 G=0.074	67.8	24[56]		1	H=0.952 E=0.021 G=0.026	88.6

* Mean value of 15 geometries retrieved from CSD[44] with AS=1,2.

** This paper, cf. ref. 54.

Appendix

The computational program for PC compatible computers is now available by sending a diskette. After writing the program the diskette will be sent back. E-mail contact may be realised by using the following address: chamis@chem.uw.edu.pl

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References

1. Pauling, L. *J. Am. Chem. Soc.* **1947**, 69, 542
2. Kruszewski, J.; Krygowski, T. M. *Tetrahedron Letters*, **1972**, 3839.
3. Krygowski, T. M. *J. Chem. Inf. Comput. Sci.*, **1993**, 33, 70.
4. Bird, C. W. *Tetrahedron*, **1985**, 41, 1414; Bird, C. W. *Tetrahedron*, **1986**, 42, 89; Bird, C. W. *Tetrahedron*, **1987**, 43, 4725; Bird, C. W. *Tetrahedron*, **1990**, 46, 5697; Bird, C. W. *Tetrahedron*, **1992**, 48, 335; Bird, C. W. *Tetrahedron*, **1992**, 48, 1992; Bird, C. W. *Tetrahedron*, **1992**, 48, 7857; Bird, C. W. *Tetrahedron*, **1993**, 49, 8441.
5. Bergmann, E. D.; Pullman, B. Eds. Aromaticity, Pseudo-Aromaticity and Anti -Aromaticity; Israel Academy of Science and Humanities: Jerusalem, 1971; Jerusalem Symp. Quant. Biochem., Vol. III.
6. Cook, M. J.; Katritzky, A. R.; Linda, P. *Adv. Heterocycl. Chem.*, **1974**, 17, 255.
7. Garratt, P. J., Aromaticity, Wiley: New York, 1986.
8. Katritzky, A. R.; Barczyński, P.; Musumurra, G.; Pisano, D.; Szafran, M., *J. Am. Chem. Soc.* **1989**, 111, 7; Katritzky, A. R.; Feygelman, V.; Musumurra, G.; Barczyński, P.; Szafran, M. *J. Prakt. Chem.* **1990**, 332, 853; Katritzky; A. R.; Feygelman, V.; Musumurra, G.; Barczyński, P.; and Szafran M. *J. Prakt. Chem.* **1990**, 332, 870; Katritzky, A. R ; Barczyński, P. *J. Prakt. Chem.* **1990**, 332, 885.
9. Jug, K; Köster, A.M. *J.Phys.Org.Chem.* **1991**, 4, 163.
10. Krygowski, T. M.; Ciesielski, A.; Bird, C. W. and Kotschy, A. *J. Chem. Inf. Comput. Sci.*, **1995**, 35, 203.
11. Cyrański, M. and Krygowski, T.M. *Pol. J. Chem.* **1995**, 69, 1088
12. Malinowski, E.R.; Hovery, D.G. Factor Analysis in Chemistry; Wiley Interscience; New York, 1980
13. Schleyer P.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem. Int. Ed.*, **1995**, 34, 337
14. Schleyer P.R., Jiao H., *Pure Appl. Chem.* **1996**, 68, 209.
15. Schleyer P.R., Maerker C., Dransfeld A., Jiao H., Eikema Hommes, N.J.R., *J. Am. Chem. Soc.* in press.
16. Krygowski, T.M.; Cyrański, M.; Ciesielski, A.; Świrska, B.; Leszczyński, P. *J. Chem. Inf. Comput. Sci.*, **1996** in press.
17. Cyrański, M.; Krygowski, T.M. *J. Chem. Inf. Comput. Sci.*, **1996** in press.
18. Katritzky, A. R.; Karelson, M.; Wells, A.P. *J. Org. Chem.* **1996**, 61, 1619

19. Krygowski, T.M.; Wisiorowski, M.; Nakata, K.; Fujio, M.; Tsuno, Y.; *Bull. Chem. Soc. Jpn.* **1996** in press.
20. Gdaniec, M.; Turowska-Tyrk, I.; Krygowski, T.M. *J. Chem. Soc. Perkin II* **1989**, 613
21. Krygowski, T.M. Anulewicz R., Pniewska, B.; Milart, P.; *J. Phys. Org. Chem.* **1991**, 4 121.
22. Krygowski, T.M.; Anulewicz R.; Milart, P.; Zimmermannn, T.; *J. prakt Chem.* **1994**, 336, 649.
23. Krygowski, T.M.; Anulewicz R.; Jarmuła, A.; Bąk, T.; Rasała, D.; Howard, S., *Tetrahedron*, **1994**, 50, 13155.
24. Anulewicz R.; Bąk, T.; Cyrański, M.; Krygowski, T.M.; Rasała, D.; Świrska, B.; *Pol. J. Chem.*, **1995**, 69 597
25. Anulewicz R.; Bąk, T.; Cyrański, M.; Krygowski, T.M.; Pawlak, D.; Pniewska, B.; Rasała, D.; Gawinecki, R. *Acta Chem. Scand.* **1995**, 49, 515.
26. Krygowski, T. M.; Cyrański, M. *Tetrahedron.* **1996**, 52, 1713.
27. Gordy, W. *J. Chem. Phys.*, **1947**, 15, 305
28. Bürgi, H. B.; *Angew. Chem.* **1975**, 7, 460.
29. Dunitz, J. D.; X-ray Analysis and the Structure of Organic Molecules.; New York ,1979.
30. Bürgi, H. B.; Dunitz, J. D.; *Acc. Chem. Res.* **1983**, 16, 153.
31. Kirby, A.J.; Jones, P.G.; *J. Am. Chem. Soc.* **1984**, 106, 6207
32. Krygowski, T. M.; Cyrański, M. *Tetrahedron.* **1996,** in preparation.
33. Strzelecka, H.; Vicente, R.; Ribas, J.; Legros, J.-P.; Cassoux, P.; Petit, P.; Andre, J.-J.; *Polyhedron*, **1991** 10, 687.
34. Le Floch, P.; Ricard, L.; Mathey, F.; *Bull. Soc. Chim. Fr.* **1994**, 131, 330.
35. Mootz, D.; Wussow, H.-G., *J. Chem. Phys.* **1981**, 75, 1517.
36. Florencio, F.; Garcia-Blanco, S. *Acta Cryst., C (Cr. Str. Comm.),* **1988**, 44, 576.
37. Blake, A.J.; Rankin, D.W.H; *Acta Cryst., C (Cr. Str. Comm.),* **1991** 47, 1933.
38. Furberg, S.; Grogaard, J.; Smedsrud, B; *Acta Chem. Scand. Ser.B*, **1979**, 33, 715.
39. de With, G.; Harkema, S.; Feil, D. *Acta Crystallogr., Sect. B,* **1976**, 32, 3178.
40. Neunhoeffer, H.; Clausen, M.; Votter, H.-D., Ohl, H.; Kruger, C.; Angermund, K.; *Liebigs Ann. Chem.* **1985**, 1732.
41. Atwood, J.L.; Krass, D.K.; Paudler, W.W., *J. Heterocycl. Chem.*, **1974**, 11, 743.
42. Coppens, P.; *Science,* **1967**, 158, 1577.
43. Ferguson, G.; Low, J.N.; Neilson, D.G.; Scrimgeour, S.N.; *Acta Cryst., C (Cr. Str. Comm.),* **1989**, 45, 1167.
44. Allen, F.H.; Davies, J.E.; Galloy, J.J.; Johnson, O.; Kennard, O.; McRae, Mitchell, E.M.; Mitchell, G.F.; Smith, J.M.; Watson, D.G. *J. Chem. Inf. Comput. Sci.* **1991**, 31, 187
45. Pahor, N.B.; Calligaris, M.; Randaccio, L.; *J. Chem. Soc., Perkin Trans.2,* **1978**, 42. Vogel, E.; Sicken, M.; Rohrig, P.; Schmickler, H.; Lex, J.; Ermer, O.; *Angew. Chem., Int. Ed. Engl.*, **1988**, 27, 411.; Haas, W.; Knipp, B.; Sicken, M.; Lex, J.; Vogel E.; *Angew. Chem., Int. Ed. Engl.*, **1988**, 27, 409.; Markl, G.; Sauer, H.; Kreitmeier, P.; Burgemeister, T.; Kastner, F.; Adolin, G.; Noth, H.; Holborn, K.; *Angew. Chem., Int. Ed. Engl.*, **1994**, 33, 1151.
46. Pelletier, M.; Brisse, F.; *Acta Cryst., C (Cr. Str. Comm.),* **1994**, 50, 1942.
47. Coggon, P.; McPhail, A.T.; *J. Chem. Soc., Dalton Trans.*, **1973**, 1888.
48. Badar, Y.; Chopra, A.K.; Dias, H.W.; Hursthouse, M.B.; Khokhar, A.R.; Ito, M.; Toube, T.P.; Wee,

B.C.L, *J. Chem. Soc., Perkin Trans.1*, **1977**, 1372.

49. Monge, M.A.; Puebla, E.G.; Elguero, J.; Toiron, C.; Meutermans, W.; Sobrado, I.; *Spectrochim. Acta*, Part A1/32, **1994**, 50,727.
50. McMullan, R.K.; Epstein, J.; Ruble, J.R.; Craven, B.M.; *Acta Crystallogr., Sect. B*, **1979**, 35, 688.
51. Nagawa, Y.; Goto, M.; Honda, K.; Nakanishi, H.; *Acta Cryst., C (Cr. Str. Comm.)*, **1987**, 43, 147.
52. Jeffrey, G.A.; Ruble, J.R.; Yates, J.H.; *Acta Cryst., C (Cr. Str. Comm.)*, **1983**, 39, 388.
53. Aouial, M.; Viallefont, P.; El Ammari, L.; *Acta Cryst., C (Cr. Str. Comm.)*, **1991**, 47, 1866.
54. Monoclinic, space group: Cc, a = 4.542 (1) A, b = 15.232(3) A, c= 9.807(2) A, β = 90.25(3) deg., Z=4, 649 reflections, R=0.0520. Further details of the crystal structure: list of structure factors, anisotropic displacement parametres, H-atom coordinates, complete geometry will be sent to the Cambridge Structural Database.
55. Jones, C.D.; Winter, M.A.; Hirsch, K.S.; Stamm, N.; Taylor, H.M.; Holden, H.E.; Davenport, J.D.; Krumkalns, E.V.; Suhr, R.G.; *J. Med. Chem.*, **1990**, 33, 416.
56. Wallis, J.D.; Dunitz, J.D.; *J. Chem. Soc., Chem. Comm.*, **1983**, 910.

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