Pergamon

Tetrahedron 54 (1998) 10153–10160

TETRAHEDRON

Analysis of C=O...H-O Interactions in Organic Crystal Structures

Sławomir Janusz Grabowski

Institute of Chemistry, University in Białystok, Al.J.Piłsudskiego 11/4,

15-443 Białystok, Poland

Received 31 March 1998; revised 15 June 1998; accepted 18 June 1998

Abstract: An analysis is given of C=O..H-O interactions in neutron diffraction organic crystal structures taken from Cambridge Structural Database. The dependence of the H..O intermolecular distance on the C=O bond length supports the concept of the valence sum rule. It was found that the Lewis-base strengths of C=O groups are close to the Lewis-acid strengths of O-H bonds within such systems.

Introduction

According to Kitaigorodski[1] intermolecular interactions in crystals may influence conformations of molecules but not valence angles and bond lengths. This is true except for strong external bonds like H-bonds. For example, it is well known that the O-H bond length strongly depends on the O..O distance in O-H..O bonds.[2] Intermolecular interactions in crystals may also influence other qualities of H-bonds, for example reducing potential barrier heights for the double proton transfer in carboxylic acid dimers.[3]

The empirical bond valence model[4] is very successful in analyzing internal and external bonds of crystal structures.[5] For example, the hydrogen-bond energy may be given by the valence of the H..O (acceptor) bond.[6]

A lot of studies deal with different correlations between geometrical parameters of H-bonds but the influence of H-bonds on bond lengths (except for D-H, D denotes the donor atom) has not yet been investigated. This paper describes the influence of H-bonds - the strong intermolecular interactions - on the C=O groups, until now thought to be insensitive to environmental effects.

The influence of the external bonds and the remaining parts of molecules (all the molecule apart from the C=O bond under consideration) on the C=O bond lengths was studied before[7] using the statistical approach proposed by Taylor and Kennard.[8] The results showed that the remaining parts of molecules influence the C=O bond lengths but intermolecular interactions (external bonds) do not. However in this paper (ref. 7) the sample of the structural data was restricted within narrow limits to the crystal structures of simple aliphatic carboxylic acids. The analysis of the C=O..H-O interactions is extended here to different kinds of compounds.

An investigation of the influence of environmental effects on the carbonyl group is of great importance; the C=O groups often form H-bonds influencing behavior in a wide variety of systems ranging from small chemical systems to biochemical ones - large macromolecules and proteins. Organic addition and elimination reactions and transformation paths of carbonyl derivatives have been investigated[9] to understand the nature of the other type of interactions, i.e. N..C=O systems.

0040-4020/98/$ - see front matter
PII: S0040-4020(98)00607-3

Selection of the Data Sample

In this paper the Cambridge Structural Database[10] was searched for crystal structures of molecules containing C=O groups involved in O-H..O bridges. The accurate neutron-diffraction data with R-values ≤ 8% and e.s.d's for bond lengths ≤ 0.005 Å were taken into account. The Database was screened for ordered and error-free structures. As the first step of analysis C=O..H-O intermolecular systems with H..O distances ≤ 2.6 Å (a little less than the appropriate sum of van der Waals radii) and O-H..O angles greater than 90° were separated. 58 such systems were found for which H..O distances range from 1.205 to 2.575 Å. To obtain a better insight into the statistical relations, this study is restricted to the C=O..H-O systems for which each C=O bond is involved in only one H..O interaction.

After such limitation the sample consists of 47 O-H..O=C systems for which O-H internal bonds range from 0.815 to 1.237 Å, C=O bonds range from 1.206 to 1.317 Å, H..O external bonds from 1.205 to 2.575 Å. Table 1 shows the geometries of C=O...H-O systems and their reference codes.

Table 1. The geometries of C=O...H-O systems of organic crystal structures found in the Cambridge Structural Database; distances in Å, angles in degrees, H..O < 2.6 Å, e.s.d's ≤ 0.005 Å, R ≤ 8 %, O-H..O angle ≥ 90°

Refcodes	O-H	H..O	O..O	O-H..O	C=O
1. ACAMCL01	1.213	1.213	2.426	180.00	1.263
2. ALXANM01	0.815	1.919	2.725	169.42	1.214
3. ALXANM01	0.815	1.965	2.779	176.70	1.218
4. AMBACO07	1.039	1.457	2.496	179.13	1.288
5. ARGIND11	0.915	1.966	2.870	169.12	1.255
6. BAMACR	0.982	2.575	3.170	119.05	1.255
7. BAMACR	0.952	2.197	2.848	124.69	1.256
8. CAMALD03	0.988	1.764	2.724	163.00	1.261
9. CAMALD03	0.974	1.820	2.791	174.33	1.255
10. CIRVAA01	0.953	1.939	2.891	176.16	1.229
11. CIRVAA01	0.953	2.008	2.932	162.99	1.229
12. CIRVAA01	0.858	1.865	2.711	168.33	1.277
13. CUHOPT04	0.973	1.694	2.658	170.50	1.216
14. DLASPA02	1.035	1.508	2.542	179.42	1.251
15. DMAHOX01	1.073	1.455	2.527	178.20	1.259
16. DOBJIN01	0.965	1.822	2.787	178.42	1.251
17. FAHCAS01	0.970	1.846	2.783	161.64	1.245
18. FEROCA12	0.996	1.636	2.632	178.38	1.226
19. FEROCA12	1.008	1.593	2.600	176.01	1.239
20. FEROCA12	1.005	1.601	2.606	179.12	1.224
21. FEROCA12	0.997	1.663	2.660	178.41	1.223

22. HDRZHO11	1.227	1.227	2.454	180.00	1.277
23. KAOXYA01	1.151	1.328	2.476	174.25	1.275
24. KDGLUM01	0.945	2.105	3.035	167.80	1.246
25. KDGLUM02	0.961	2.317	2.955	123.27	1.232
26. KHDASL01	1.224	1.224	2.449	179.98	1.283
27. KHMTAR01	1.220	1.220	2.440	180.00	1.279
28. KHMTAR01	0.971	2.451	2.944	111.10	1.206
29. KHMTAR01	1.237	1.237	2.475	180.00	1.278
30. KHMTAR01	0.955	1.826	2.771	170.05	1.261
31. KHMTAR01	0.948	1.776	2.706	166.36	1.256
32. LGLUAC03	1.024	1.568	2.581	169.31	1.268
33. LIHPAL01	1.122	1.294	2.404	168.87	1.276
34. LIHPAL01	1.195	1.205	2.394	171.88	1.289
35. LIHPAL01	0.970	2.495	3.173	126.86	1.294
36. LIHPHM01	1.195	1.205	2.393	171.31	1.284
37. LIHPHM01	1.173	1.226	2.388	169.28	1.269
38. LIHPHM01	0.960	1.876	2.834	174.72	1.235
39. MALAQZ01	0.955	1.847	2.787	167.35	1.221
40. NALCYS02	1.036	1.513	2.549	178.37	1.247
41. NRURAM11	0.955	1.956	2.846	154.22	1.224
42. PYOTCA01	1.148	1.284	2.430	174.92	1.267
43. RBHOXY01	1.225	1.225	2.446	174.52	1.317
44. SUBRAC01	1.009	1.631	2.638	175.99	1.226
45. SUCACB02	0.994	1.688	2.678	173.68	1.222
46. UREAOH12	0.994	1.669	2.648	167.61	1.255
47. ZZZFQQ02	0.937	1.845	2.761	164.99	1.232

The correlations within C=O..H-O systems

The final sample consists of 47 C=O..H-O systems. The more detailed characterisation of the sample is given in Table 2. The data are divided into subsets with increasing H..O distance. Apart from the entries existing for the range 2.2-2.6 Å (Table 2), one can see that the mean O-H bond lenghts and the mean O-H..O angles increase with decreasing H..O distances. It is well known and in line with the previous investigations.[2,6] The existence of only four systems for the range of 2.2-2.6 Å for H..O external bonds, is the result of the choice of the sample. The systems for which C=O groups are involved in only one H..O interaction are taken into account in this paper and C=O groups may be involved in not only one H-bond (if H..O distances are longer). The producing of more than one hydrogen bond by weakly bonding anions has already been described in detail.[11]

Table 2. Mean values of the C=O bond and of the other geometrical parameters of C=O..H-O systems for given H..O intervals, standard errors (standard uncertainties) are given in parentheses,[a] distances in Å, angles in degrees

H...O [Å]	n [b]	⟨ O-H ⟩	⟨ H...O ⟩	⟨ C=O ⟩	⟨O-H..O⟩
< 1.4	12	1.19 (1)	1.24 (1)	1.280 (4)	175.4 (1.3)
1.4 - 1.8	15	1.008 (8)	1.61 (3)	1.244 (5)	174.2 (1.4)
1.8 - 2.2	16	0.931 (1)	1.93 (3)	1.241 (4)	166.3 (3.2)
2.2 - 2.6	4	0.971 (4)	2.46 (5)	1.25 (2)	120.1 (3.4)
all	47	1.03 (2)	1.70 (5)	1.252 (4)	167.2 (2.5)

[a] standard errors se⟨x⟩ of the mean values ⟨O-H⟩, ⟨H...O⟩, ⟨C=O⟩ and ⟨O-H..O⟩ are calculated according to the relation $se\langle x\rangle = [\ \Sigma_i (x_i - \langle x\rangle)^2 / n (n - 1)\ ]^{0.5}$

[b] n - number of C=O..H-O systems for the given interval

Table 2 also shows that a decrease of the length of H..O is associated with an increase of C=O. It is particularly evident for the H..O contact less than 1.4 A compared with H..O distances in the range 1.4-1.8 Å; one can observe a shortening of the average C=O bond from 1.280 to 1.244 Å, the difference between these values is greater than 3σ.

Table 3 lists the mean C=O and H..O distances for different subsets of the data considered here. The sample of 47 C=O..H-O systems (sample 1 in Table 3) contain two major types of proton acceptors; C=O bonds and COO^- groups (samples 2 and 3 respectively). The sample 2 does not contain the data of bis(acetamide) hydrochloride (ACAMCL01 refcode in Table 1) for which there is no typical C=O..H-O system, but rather C=O..H^+..O=C (the same data as for the sample 2 but after the inclusion of ACAMCL01 are also given and designated as the sample 2*). The mean H..O and C=O distances for the sample 3 are 1.40(6) and 1.273(4) Å respectively, while the corresponding values for the sample 2 are 1.72(8) and 1.231(5) Å showing the greater basicity of the COO^- acceptor than the basicity of C=O.

Table 3. Mean C=O and H..O distances for different samples, standard errors are given in parentheses (calculated in the same way as in Table 2), distances in Å

	Sample	n	mean C=O	mean H..O
1	all data	47	1.252(4)	1.70(5)
2	O-H..O=C systems	12	1.231(5)	1.72(8)
2*	the same as sample 2 but with ACAMCL01	13	1.233(5)	1.68(9)
3	COO^-..H^+..COO^- and COOH ..$^-$OOC systems	17	1.273(4)	1.40(6)
4	H_2O as donors, C=O and COO^- as acceptors	17	1.246(5)	2.00(6)

The sample 4 of Table 3 represents the C=O..H-O systems with water molecules as proton donors and COO^- or C=O groups as proton acceptors. Because of the great variability of the geometry of water molecules in crystals depending not only on H-bond formation,[12] the sample 4 is not analyzed here. It is worth mention that C=O and H..O mean distances for COO^-... H_2O systems (13 cases) are 1.248(6) and 2.05(8) Å whereas the corresponding values for C=O...H_2O systems (4 cases) are 1.238(6) and 1.87(3) Å. The longer mean C-O bond

length for $COO^-..H_2O$ systems than for C=O..H_2O is justified but the longer corresponding mean H..O distance is not.

Fig 1 shows the plot of C=O bond length against H..O distance for the experimental data taken from the Cambridge Structural Database. 30 entries are taken into account, being the sum of the two samples (2* and 3 of the Table 3).

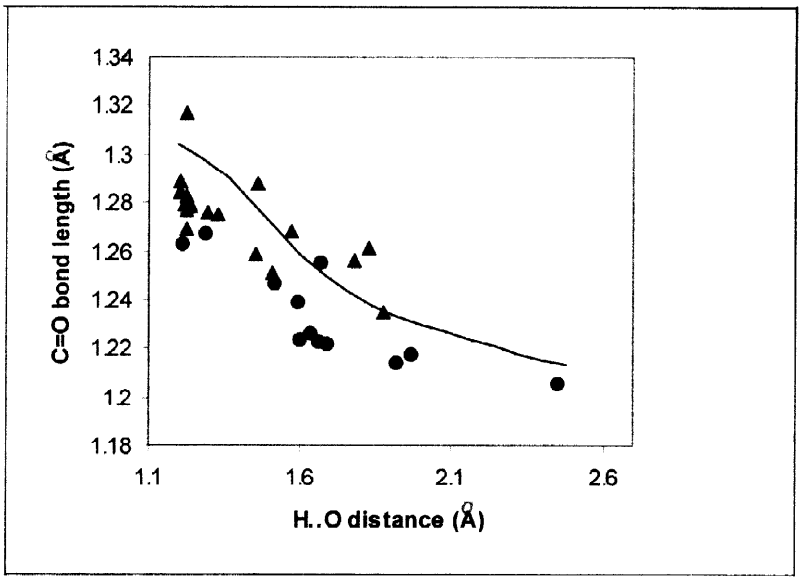

Fig 1. Correlation between the C=O bond length and H..O distance of C=O..H-O systems (angle at H > 90°, H..O < 2.6 Å) for experimental data; circles (2* sample of Table 3), triangles (sample 3 of the same Table), the continuous curve (theoretical results - see the next Section)

The linear regression coefficient for the dependence between C=O and H..O for sample 2 is -0.768 and for the sample 3 -0.732. So if a significant correlation exists it is non-linear. The Spearman-rank-correlation[13] coefficient r_s was calculated to be -0.825 and -0.787 for samples 2 and 3 respectively (and -0.857 for 2*). The values of r_s exclude for an appropriate test the null hypothesis of zero correlation at the 1% significance level. It means that the reliability of the correlation between C=O bond length and H..O distance within C=O..H-O systems for samples 2 and 3 is greater than 99%.

The use of the valence sum rule to C=O..H-O systems

The observed scatter-plot (Fig 1) is compared with the analytical curve of the form (Fig 1, continuous curve):

$$s_{C=O} + s_{H..O} = 2 \qquad (1)$$

where

$$s_{C=O} = \exp [(R^o_{C-O} - R_{C=O})/ B] \qquad (2)$$

$s_{C=O}$ and $s_{H..O}$ correspond to the valences of C=O internal and H..O external bonds respectively, $R_{C=O}$ is the length of the C=O bond; R^o_{C-O} is the reference length of the single C-O bond [14] (1.428 Å taken from electron

diffraction data for methanol), B equals 0.316. The constant B may be determined from eq. 2 if we fix the value of s for the given known length of the internal or external bond R. In this paper B was determined from the length of the double C=O bond taken from electron diffraction data for acrolein [15] (r=1.209 A, s = 2). One can write the appropriate equation exp[(1.428-1.209)/B]=2 from which constant B is calculated.
The Equation (1) expresses the idea of the valence sum rule:[6]

$$V_i = \Sigma\, s_{ij} \qquad (3)$$

The valence V_i of i-th atom is assumed to be shared between the bonds it forms. s_{ij} is the valence of the bond between atoms i and j. It has been found that the bond valence correlates inversely with the bond length. Such relation may be approximated by exponential equation (Eq. 2 of this paper) or by:

$$s_{ij} = (R_{ij}/R_o)^{-N} \qquad (4)$$

R_o, N are fitted constants, R_o being the length of the bond of unit valence and R_{ij} is the length of the bond under consideration. Eq.1 refers to the atomic valence of oxygen atom of C=O bond which should be equal to 2 (the oxidation state).

The correlation between bond valence and bond length can be approximated by an exponential function of the form presented above but over the limited range of bond lengths. The situation is more complicated for H-O bonds (both external and internal) which cover the whole range of valences between 0 and 1.0 v.u. (v.u. - valence units).[11] $s_{H..O}$ values used in Equation (1) were taken from the dependence between O-H bond length and its valence applying over the whole range of internal and external bonds. [11]

The curve obtained from Eq. (1) (Fig 1, the continuous line) agrees with the experimental results (Fig 1, circles and triangles) in spite of the simplicity of the relation used here.

H..O contact versus O-H bond

The same manner as that presented above was used for the well known dependence between H..O external and O-H internal bonds. Fig 2 presents the experimental data for the sample of 34 C=O..H-O systems considered in previous sections (the systems with O-H bond lengths > 0.957 Å were taken into account). The continuous curve at Fig 2 was constructed from the valence sum rule:

$$s_{O\text{-}H} + s_{H..O} = 1 \qquad (5)$$

s-values were obtained according to ref. 11. Fig 2 shows that the influence of the H..O contacts within C=O..H-O systems is stronger on O-H bonds than on C=O carbonyl groups. The agreement between the experimental data (Fig 2, circles) and the relation predicted from Eq. 5 (Fig 2, the continuous line) is excellent in spite of the data based on the O-H..O=C systems belonging to different kinds of compounds. A similar theoretical relation but only between H..O and O-H within narrow limits of O-H..O bonds was investigated earlier[16,17] using the idea of bond number conservation. The relation of bond number conservation[18] is based on the idea of bond number introduced by Pauling[19] and applied later in many chemical problems[20]. It is similar to the bond valence model and the valence sum rule.

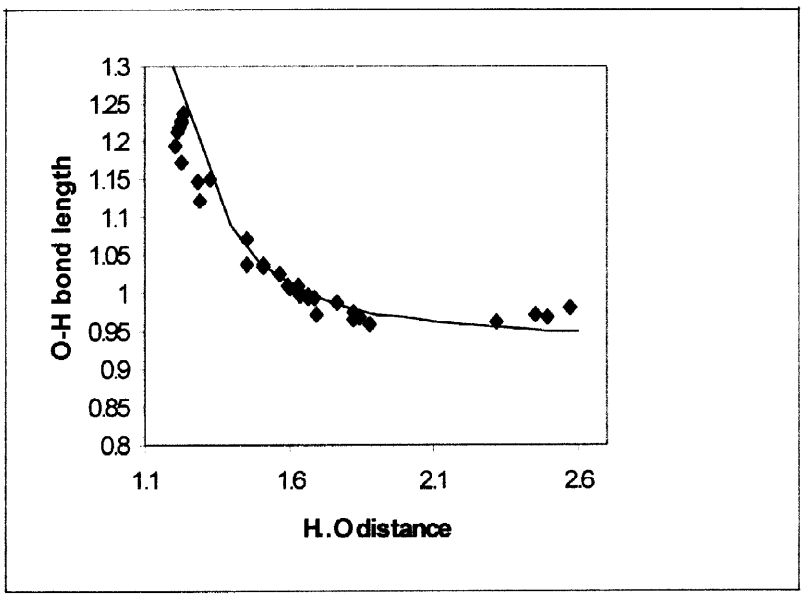

Fig 2. Correlation between the O-H bond length and the H..O distance; for experimental data (squares), and the theoretical curve obtained from Eq.5 (the continuous line)

Acidities of O-H and basicities of C=O bonds

Fig 3 shows the plot of O-H acidities versus C=O basicities. The Lewis acidity of O-H bond is connected with its length. Elongation of the O-H bond causes a decrease of its valence (below unity) and an increase of its acidity s_a which can be calculated as $s_a = (1 - s_{OH})$.

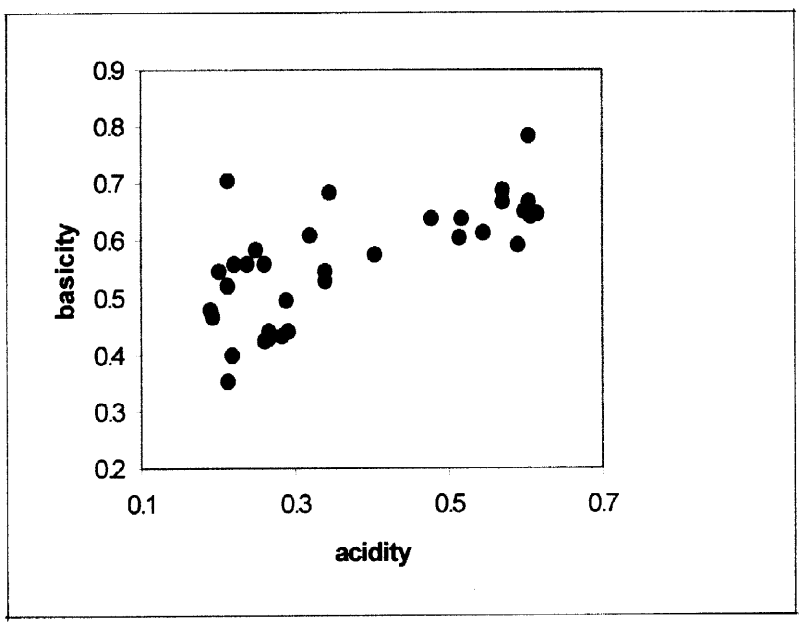

Fig 3. O-H acidities vs. C=O basicities within C=O...H-O systems taken from the Cambridge Structural Database

The Lewis basicity of C=O bond increases with the elongation of its length (with the decrease of its valence). The basicity of C=O may be calculated as $s_b = (2 - s_{C=O})$; $s_{C=O} = 2$ corresponds to the valence of C=O

double bond (not elongated). The linear regression coefficient for the dependence between O-H acidity and C=O basicity is 0.692, so there is no strong correlation between them but the results show that bonds may be formed if the Lewis-acid strength of the electron acceptor is close to the Lewis-base strength of the electron donor.[21] This is in line with the other investigations concerning H-bonds in crystal structures.[22,23] It is worth mention that the Spearman-rank correlation coefficient r_s for the dependence presented at Fig 3 is 0.646, the value of r_s excludes the hypothesis of zero correlation at 1% significance level.

Acknowledgements

The author expresses his sincere thanks to Professor I.D.Brown of McMaster University, Canada, for stimulating conclusions and discussions.
The author wishes to thank Professor T.M.Krygowski of Warsaw University for the conclusions of the manuscript and for access to the Cambridge Structural Database.

REFERENCES

1. Kitaigorodski, A.I. *Molecular Crystals and Molecules*, Academic Press, New York, 1973.
2. Ichikawa, M. *Acta Cryst.*, **1978**, *B34*, 2074, and references cited therein
3. Hayashi, S.; Umemura, M.; Kato, S.; Morokuma, K. *J.Phys. Chem.*, **1984**, *88*, 1330. Grabowski, S.J.; Krygowski, T.M. *Chem.Phys.Lett.*, **1988**, *151*, 425.
4. Brown, I.D. *Chem.Soc.Rev.*, **1978**, *7*, 359.
5. Brown, I.D. *Acta Cryst.*, **1992**, *B48*, 553, and references cited therein
6. Brown, I.D. *Acta Cryst.*, **1976**, *A32*, 24, and references cited therein
7. Grabowski, S.J. *J.Chem.Res.*, **1988**, 252.
8. Taylor, R.; Kennard, O. *Acta Cryst.*, **1983**, *B39*, 517.
9. Cieplak, A.S. *Organic Addition and Elimination Reactions; Transformation Paths of Carbonyl Derivatives*, in *Structure Correlation*, Bürgi, H.-B.; Dunitz, J.D. Eds. VCH, Weinheim, 1994.
10. Allen F. H.; Bellard S.; Brice M. D.; Cartwright B. A.; Doubleday A.; Motherwell W.D.S.; Rodgers J.R.; Watson D. G.; *Acta Cryst.* **1979**, *B35*, 2331. *Cambridge Structural Database System*, User's Manual, Part I,II,III, CCDC, Cambridge, **1989.** Allen, F.H.; Davies, J.E.; Galloy, J.E.; Johnson, J.J.; Kennard, O.; Macrae, C.F.; Mitchell, E.M.; Mitchell, G.F.; Smith, J.M.; Watson, G.D. *J.Chem.Inf.Comput.Sci.*, **1991**, *31*, 187.
11. Brown, I.D. *Can.J.Phys.*, **1995**, *73*, 676.
12. Krygowski, T.M.; Grabowski,S.J.; Konarski,S. Tetrahedron, submitted
13. Sachs, L. *Angewandte Statistik*, Springer-Verlag, Berlin, 1992.
14. Kimma, K; Kubo,M. *J.Chem.Phys.*, **1959**, *30*, 151.
15. Kuchitsu, K.; Fukuyama, T.; .Morimo, Y. *J.Mol.Struct.*, **1969**, *4*, 41.
16. Grabowski, S.J. *Croatica Chem. Acta* **1988**, *61*, 815.
17. Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J.Am.Chem.Soc.*, **1994**, *116*, 909.
18. Johnston, H.S. *Adv.Chem.Phys.*, **1960**, *3*, 131.
19. Pauling, L. *J.Am.Chem.Soc.*, 1947, *69*, 542.
20. Bürgi, H.-B.; *Angew. Chem.*, **1975**, *7*, 460; Krygowski, T.M.; Cyrański, M. *Tetrahedron*, **1996**, *52*, 10255. Grabowski, S.J.; Krygowski, T.M. *Tetrahedron*, **1998**, *54*, 5683.
21. Brown, I.D. *J.Chem.Soc., Dalton Trans.*, **1980**, 1118.
22. Etter, M.C. *Acc.Chem.Res.*, **1990**, *23*, 120.
23. Hanton, L.R.; Hunter, C.A.; Purvis, D.H. *J.Chem.Soc., Chem.Commun.*, **1992**, 1134.