

T.M. Krygowski · J.E. Zachara

How π -electron delocalisation reflects replacement of H^+ with Li^+ in variously substituted malonaldehydes

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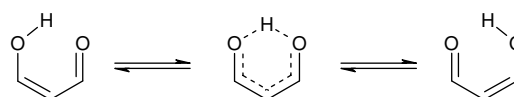
Abstract Correlations were studied between the properties of Bader's ring and bond critical points calculated for variously substituted malonaldehyde (containing intramolecular H-bond) and its π -electron delocalisation expressed by aromaticity indices HOMA and NICSs. It was observed that π -electron delocalisation of the system strongly depends on the substituent and its position. Replacement of the H^+ with Li^+ in malonaldehyde allowed us to study the role of unoccupied 2p orbital in π -electron delocalisation. In the case of lithium system the aromaticity is increased as compared with the malonaldehyde itself and moreover with the malonaldehyde anion. This proves that the unoccupied 2p orbital of Li^+ may play a significant role in delocalisation of π -electrons due to its low orbital energy. In the case of lithium system the substituent effect is negligible, which resembles the situation in benzene derivatives.

Keywords Malonaldehyde · π -Electron delocalisation · Intramolecular H-bond · Ab initio calculations · Aromaticity

1 Introduction

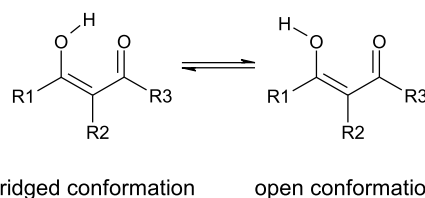
Hydrogen bonded systems are widely studied since those interactions are ubiquitous in the world around us [1–4]. Malonaldehyde is one of the most useful model systems for studying the properties of intramolecular H-bonding. A particular value of this system stems from the presence of two neutral donor and acceptor oxygen atoms connected by a π -electron spacer (Scheme 1).

The equivalence, presented in Scheme 1, may be easily perturbed in a controlled way by introducing different sub-



Scheme 1 Structures of enol form of malonaldehyde

stituents at carbon atoms of the spacer. In a series of papers, Grabowski [5–7] investigated the substituent effect on the strength of intramolecular H-bond for malonaldehyde substituted in various ways by chlorine and fluorine depicted in Scheme 2 as R1, R2 and R3. A good monotonic relationship between the H-bond energy and the electronic densities at the bond critical point of $H \cdots O$ bond was reported [5].



Scheme 2 Structural scheme of studied malonaldehyde derivatives

Further application of Bader's AIM theory [8,9] for a wider number of systems supported this observation; it has also been shown that electron density in the quasi-ring (spacer and the $OH \cdots O$ fragment) correlates nicely with the H-bond strength estimated as a difference between the energy of the closed and open conformations of the enol form of malonaldehyde (Scheme 2). The π -electron delocalisation in the spacer became a subject of interest [7] since the enol tautomeric form of malonaldehyde is a typical system for Gilli's resonance-assisted H-bonds [10, 11]. Application of the modified resonance parameter for the π -electron spacer has shown that it is well correlated with the net hydrogen atomic charge of the hydrogen within $O-H \cdots O$ bond, and with electron density at $H \cdots O$ bond critical point.

The aim of this paper is to study the relationship between the substituent effect and π -electron delocalisation in the spacer expressed by aromatic indices like Nucleus Independen-

Dedicated to Prof. Karl Jug on the occasion of his 65th birthday anniversary.

T.M. Krygowski (✉) · J.E. Zachara
Department of Chemistry, Warsaw University,
Pasteura 1, 02-093 Warsaw, Poland
E-mail: tmkryg@chem.uw.edu.pl
Tel.: +48-22-8222892
Fax : +48-22-8222892

dent Chemical Shift (NICSs) [12, 13], Harmonic Oscillator Model of Aromaticity (HOMA) [14–16] and its extension on EN and GEO terms [17, 18]. Following the Hellmann–Feynman theorem [19], distribution of electronic density in the molecule determines the forces acting on the nuclei, which in turn define the geometry of the molecule in question. Thus geometry may provide reliable information about electron distribution and, employing appropriate references, it may be used to describe π -electron delocalisation. Aromaticity indices like HOMA or NICS describe π -electron delocalisation for cyclic systems. In the case of HOMA, cyclicity is not necessary – the index, still named aromaticity index, may be used to quantify π -electron delocalisation even if it is applied for linear π -electron species. In the present report HOMA will be used in this sense.

Moreover, the H-bonding effect on the π -electron delocalisation in the spacer in enol form of malonaldehyde seems to be mostly due to the electrostatic effect of H^+ on the electron structure, since the energy of the empty 2p orbital is very high. To study the role of the unoccupied 2p orbital and its energy on delocalisation in malonaldehyde, the analysis of data for the case when H^+ is replaced with Li^+ was carried out. Since the acetylacetone derivatives are very similar to the systems discussed in our report, some earlier work should be mentioned. 1H -NMR spectroscopy studies on various metal chelates of acetylacetone and its derivatives [20] suggested no traces of aromatic-like properties in these systems. Recently, the keto–enol tautomerisation of acetylacetone has been studied indicating a dependence of the π -electron structure on the localisation of proton [21].

2 Definitions and computational details

Aromaticity index HOMA [14, 22] is based on geometry parameters of the π -electron moiety and is defined as follows:

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum (R_{opt} - R_i)^2, \quad (1)$$

where n is the number of bonds taken into the summation; α is a normalisation constant (for CC and CO bonds α is 257.7, 157.38, respectively) fixed to give HOMA = 0 for a model non-aromatic system, for example, Kekulé structure of benzene [23] and HOMA = 1 for the system with all bonds equal to the optimal value R_{opt} assumed to be realized for full aromatic systems (for CC and CO bonds R_{opt} is equal to 1.388 and 1.265 Å, respectively); R_i stands for a running bond length.

The HOMA index may also be analysed in its form with the separation of two structural effects decreasing aromaticity: (1) an increase of mean bond length and (2) an increase of bond length alternation [17, 18] according to the Eq. (2).

$$\begin{aligned} \text{HOMA} &= 1 - \left[\alpha (R_{opt} - R_{av})^2 + \frac{\alpha}{n} \sum_i (R_{av} - R_i)^2 \right] \\ &= 1 - \text{EN} - \text{GEO}, \end{aligned} \quad (2)$$

where EN term describes the decrease of aromaticity due to bond elongation, whereas GEO term – the decrease due to an increase of bond alternation, R_{av} stands for average bond length.

NICS [12, 13] is defined as a negative value of the absolute shielding estimated in the centre of the aromatic moiety in question, whereas NICS(1) [24] – 1 Å above the centre.

HOMA, GEO, EN and NICSs values for variously substituted malonaldehyde were calculated using geometry data obtained by Grabowski [5].

Ab initio modelling was applied to the anion and lithium salt of malonaldehyde using Gaussian98 [25]. Geometry optimisations were performed at the MP2/6–311++G** level of theory and the results were used to calculate the HOMA, GEO and EN values. The NICSs values were calculated at the HF/6–311++G** level of theory using the GIAO method and employing DIAMOND ver. 2.1e [26] for estimating geometric centre for the O–C–C–O fragment.

3 π -electron delocalisation in the spacer of enol form of malonaldehydes

Table 1 presents the values of HOMA, EN and GEO for variously substituted malonaldehyde calculated from geometry [5], as well as NICS and NICS(1), the electronic density (in e/a_o^{-3}) and Laplacian (in e/a_o^{-5}) in the bond critical points (BCP) of O–H and H \cdots O and in the ring critical point (RCP). All of them are obtained from the optimisation at MP2/6–311++G** level of theory [5–7].

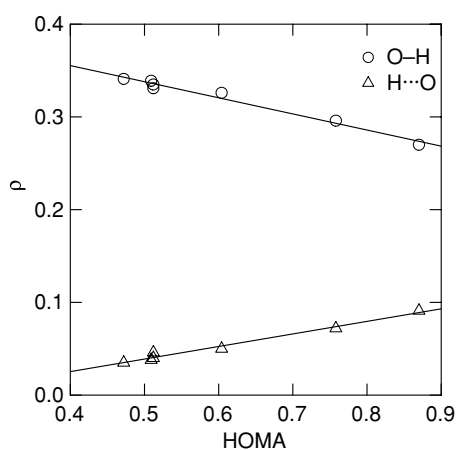
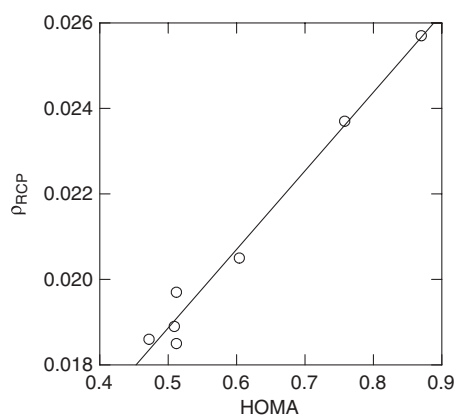
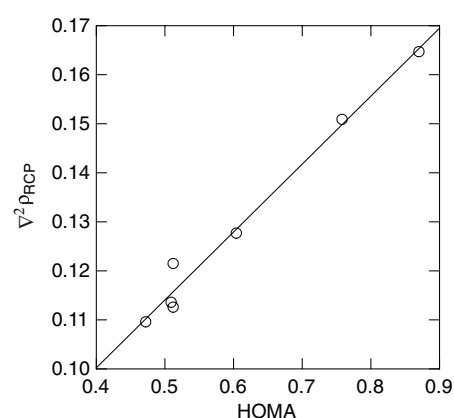
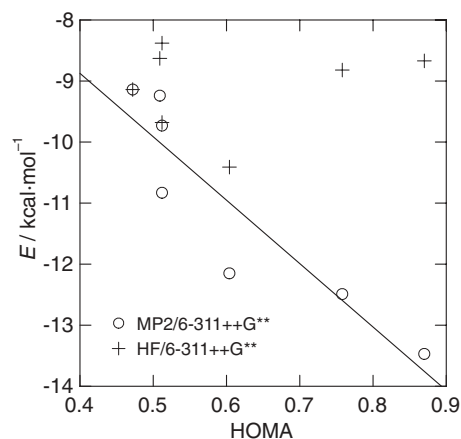
Analysing HOMA values and its components (Table 1), it is clear that the dominant contribution to the variation in HOMA comes from the changes in bond length alternation (GEO term), whereas the EN term is almost negligible. When electron densities in BCP of O–H and H \cdots O, the ρ_{O-H} and $\rho_{O\cdots H}$ are plotted against HOMA, the scatter plots are as presented in Fig. 1.

Also, the dependences of electron density and its Laplacian in the RCP on HOMA values are surprisingly good, as shown in Figs. 2 and 3. This means that π -electron delocalisation which is undoubtedly monitored by electron density and its Laplacian in the RCP is well correlated with the geometry-based index HOMA (correlation coefficient: 0.99). Similar relationships, although slightly worse, were found for 18 individual rings in 10 benzenoid hydrocarbons [27].

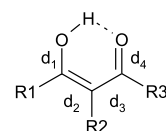
The HOMA values are also well correlated with the energy of intramolecular H-bond calculated as a difference between the energy of bridged and open conformers of enol form of malonaldehyde (Scheme 2). Figure 4 presents this relationship. Interestingly, if the computations are carried out at the HF/6-311++G** level of theory, thus taking into account electron correlation only as an averaged electrostatic field, there is practically no reasonable relationship. When the MP2/6-311++G** level of theory is employed, that takes into account electron correlation, improvement is remarkable and the correlation is quite acceptable, with $cc = -0.91$.

Table 1 Labelling of the variously substituted derivatives of malonaldehyde (Scheme 3); values of HOMA, EN and GEO; values of NICS and NICS(1); values of electronic density (in e/a_0^{-3}) and Laplacian (in e/a_0^{-5}) in bond critical points of O–H and O \cdots H and in ring critical points, resonance parameter Δ_{rp} as well as energy of intramolecular H-bond

substituents			HOMA	EN	GEO	NICS	NICS(1)	ρ_{O-H}	$\rho_{H\cdots O}$	$\nabla^2\rho_{H\cdots O}$	ρ_{RCP}	$\nabla^2\rho_{RCP}$	Δ_{rp}	$E_{MP2}/\text{kcal}\cdot\text{mol}^{-1}$	$E_{HF}/\text{kcal}\cdot\text{mol}^{-1}$
R1	R2	R3													
H	H	H	0.604	0.067	0.328	1.755	-0.874	0.326	0.050	0.139	0.021	0.128	0.339	-12.15	-10.41
H	F	H	0.512	0.057	0.431	-0.532	-1.439	0.335	0.040	0.123	0.019	0.113	0.278	-9.73	-8.38
H	Cl	H	0.512	0.081	0.407	0.455	-1.217	0.331	0.046	0.135	0.020	0.122	0.308	-10.83	-9.68
H	H	F	0.472	0.032	0.496	-0.582	-1.346	0.341	0.035	0.116	0.019	0.110	0.237	-9.14	-9.14
H	H	Cl	0.509	0.041	0.450	0.324	-1.171	0.339	0.038	0.122	0.019	0.114	0.261	-9.24	-8.63
F	H	H	0.870	0.024	0.106	-1.090	-1.791	0.270	0.091	0.139	0.026	0.165	0.627	-13.47	-8.67
Cl	H	H	0.758	0.050	0.192	0.577	-1.344	0.296	0.072	0.150	0.024	0.151	0.471	-12.49	-8.82

**Fig. 1** Dependences of electron density in BCP of O–H bond (circles) and O \cdots H bond (triangles) on HOMA values for variously substituted derivatives of malonaldehyde. Correlation coefficients are -0.989 and 0.990 , respectively**Fig. 2** Dependence of electron density in RCP on HOMA values for variously substituted derivatives of malonaldehyde. Correlation coefficient = 0.991 **Fig. 3** Dependence of Laplacian of electron density in RCP on HOMA values for variously substituted derivatives of malonaldehyde. Correlation coefficient = 0.991 **Fig. 4** Dependence of H-bonding energy on HOMA values calculated at two levels of theory: HF/6-311++G** and MP2/6-311++G** for variously substituted derivatives of malonaldehyde. Correlation coefficient for the latest relationship is -0.913

π -electron delocalisation in the resonance assisted H-bonds (RAHB) is well described by Gilli resonance parameter [10] $Q = q_1 + q_2$, where $q_1 = d_1 - d_4$ and, $q_2 = d_2 - d_3$ (Scheme 3). The smaller is Q value the greater is π -electron delocalisation.

**Scheme 3**

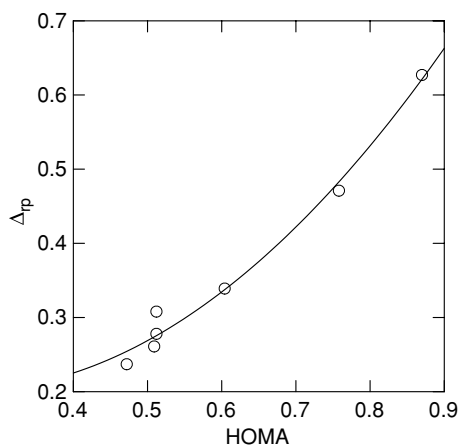


Fig. 5 Dependence of resonance parameter Δ_{rp} of the spacer and HOMA values for variously substituted derivatives of malonaldehyde; correlation coefficient for quadratic relationship is 0.990

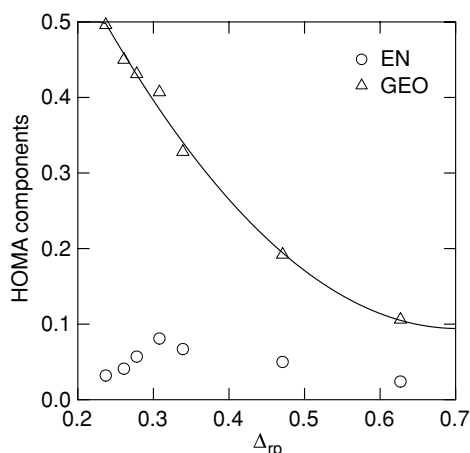


Fig. 6 Dependence of HOMA components, the EN and GEO terms, on Δ_{rp} for variously substituted derivatives of malonaldehyde

A similar resonance parameter, Δ_{rp} , has been defined by Grabowski [7]:

$$\Delta_{rp} = \frac{1}{2} \left[\frac{(\Delta d_1^o - \Delta d_1^c)}{\Delta d_1^o} + \frac{(\Delta d_2^o - \Delta d_2^c)}{\Delta d_2^o} \right],$$

where $\Delta d_1^o = d_3^o - d_2^o$ and $\Delta d_2^o = d_4^o - d_1^o$ are defined for open conformation (Scheme 2) and analogically $\Delta d_1^c = d_3^c - d_2^c$, $\Delta d_2^c = d_4^c - d_1^c$ for the closed H-bonded system (bridged conformation). In all cases d_i stands for bond length as in Scheme 2. The Grabowski index Δ_{rp} describes the π -electron delocalisation as a consequence of the formation of an intramolecular H-bond. To define Δ_{rp} parameter the geometry of the so-called 'open conformation' is needed—a situation when the intramolecular H-bond does not exist and this system is a reference state. Figure 5 presents the dependence of Δ_{rp} on HOMA values for seven molecules presented in Table 1. The correlation looks like a quadratic one since the Δ_{rp} is linear in bond lengths, whereas HOMA – quadratic. The exceptionally good correlation is not sur-

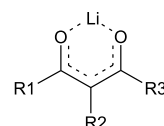
prising, since both parameters stem from the same geometric data set.

The relationship presented in Fig. 6 shows that only the alternation term (GEO) is responsible for the correlation, whereas the EN term describing bond elongation does not play any important role.

It seems to be clear that aromaticity indices, which are also the π -electron delocalisation descriptors, vary substantially depending on the character of substituents and their location in the spacer. A remarkable substituent effect is visualised in the range of variation of HOMA and NICSs values (Table 1). For NICS and NICS(1) values no such correlations as those observed for HOMA values were found. This is probably because the position of the centre of ring current in these systems is not defined precisely enough.

4 π -electron delocalisation in the spacer of enol form of malonaldehyde where H^+ is replaced by Li^+

Replacement of proton by lithium cation in the enol form of malonaldehyde (Scheme 4) leads to dramatic changes in the behaviour of π -electron delocalisation in the spacer. Li^+ is located almost centrally between the two oxygen atoms – the position depends only slightly on the nature of the substituent and the place of its attachment.



Scheme 4 Structural scheme of lithium salt of malonaldehyde derivatives

Table 2 presents the data based on the MP2/6–311++G** computations of Li^+ analogues of the enol form of malonaldehyde as well as the data for malonaldehyde anion – the analogues of those presented in Table 1.

Replacement of H^+ with Li^+ in the enol form of malonaldehyde derivatives increases dramatically π -electron delocalisation (Fig. 7). HOMA values for all substituted derivatives are now always above 0.93. Significantly weaker is π -electron delocalisation in the malonaldehyde anion, where

Table 2 Labelling of the variously substituted derivatives of lithium salt and anion of malonaldehyde; values of HOMA, NICS and NICS(1)

substituents			lithium salt			Anion		
R1	R2	R3	HOMA	NICS	NICS(1)	HOMA	NICS	NICS(1)
H	H	H	0.942	-1.139	-2.437	0.809	-1.734	-1.686
H	F	H	0.971	-2.069	-2.817	0.891	-2.534	-2.337
H	Cl	H	0.932	-2.077	-2.627	0.799	-2.425	-1.717
H	H	F	0.927	-3.485	-2.636	0.741	-4.750	-2.121
H	H	Cl	0.933	-2.297	-2.466	0.671	-5.148	-2.076
F	H	H	0.929	-3.488	-2.741	0.741	-4.756	-2.123
Cl	H	H	0.933	-2.289	-2.473	0.672	-5.146	-2.076

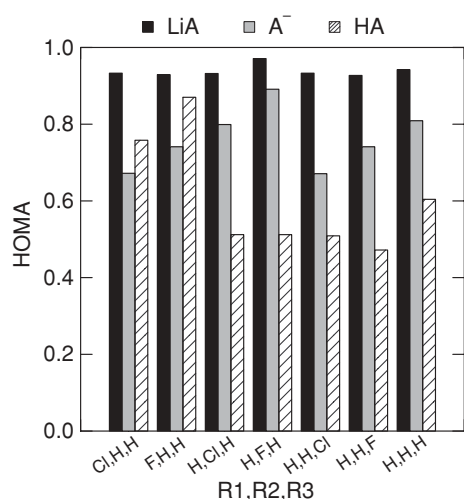


Fig. 7 HOMA values for variously substituted derivatives of lithium salt of malonaldehyde (LiA), malonaldehyde anion (A^-) and malonaldehyde (HA)

the Coulombic repulsion requires dispersion of the charge at two ends of the chain – HOMA is between 0.67 and 0.89. The highest HOMA value is for H,F,H-derivative, where the centrally located fluorine atom withdraws part of the negative charge leading to a lower electron density along the chain and less charge at both ends. The lowest π -electron delocalisation is observed for malonaldehydes with the intramolecular H-bonding. The position of substituents is again decisive.

Another interesting finding is that in the Li^+ salts the range of variability of HOMA values is about tenfold smaller than in the enol form of malonaldehyde and their magnitudes correspond to the strongly aromatic systems. The low sensitivity of π -electron delocalisation in Li^+ salt of malonaldehyde on substituent effect corresponds nicely to the situation known for monosubstituted benzene derivatives as it has been found recently [28,29]. It might be concluded that an increase of aromaticity of π -electron systems is associated with a decrease of the substituent effect.

Application of NICS and NICS(1) does not give clear results. It is not obvious how to find the best centre of the ring current, and hence the results are less decisive. Nevertheless, the overall picture is similar to that shown by HOMA, but π -electron delocalisation exhibited is lower. The most aromatic or rather quasi-aromatic [30] are lithium salts – mean NICS(1) value is -2.6 , whereas for anions is -2.0 and for the malonaldehydes -1.3 .

5 Conclusions

The BCP of the O–H and H...O bonds as well as the RCP calculated for variously substituted malonaldehyde correlate well with aromaticity index HOMA. Also, a fairly good correlation is found for the estimated intramolecular H-bond energy calculated at the MP2/6–3111++ G** level of theory.

In these cases the substituent effect on π -electron delocalisation is remarkable.

Replacement of H^+ with Li^+ in the enol form of malonaldehyde increases significantly π -electron delocalisation in the spacer expressed by HOMA and decreases remarkably the substituent effect. This is due to lower energy of the unoccupied 2p orbital for Li^+ as compared with H^+ , which may facilitate delocalisation of π -electrons. The aromaticity of malonaldehyde anion is smaller than that for lithium derivatives, and this proves that lithium 2p orbital plays an important role in π -electron delocalisation.

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