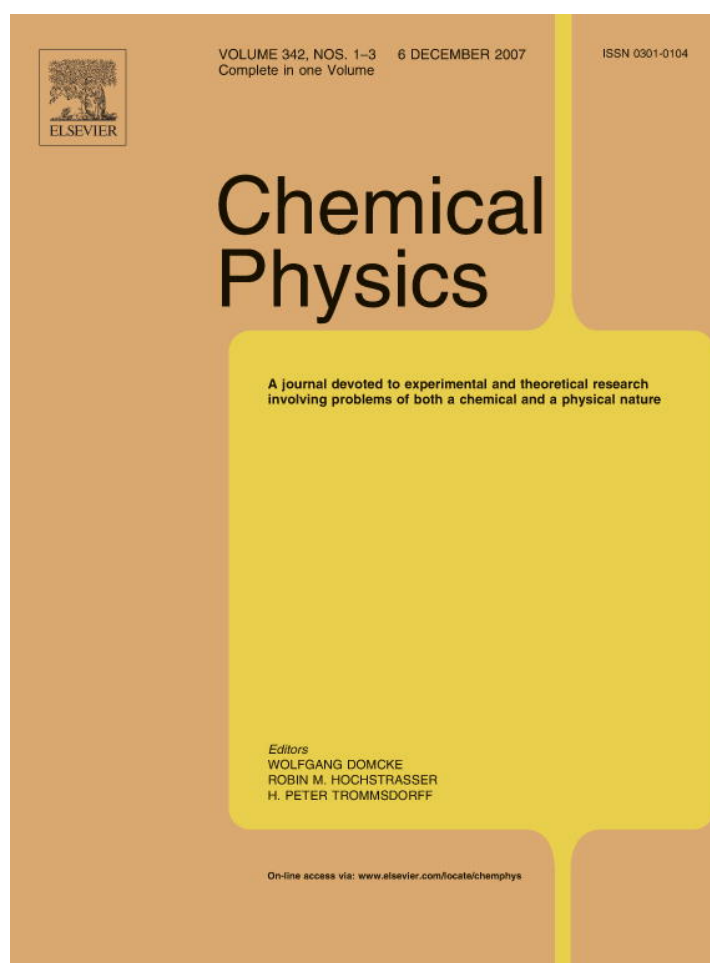


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# The proton transfer reaction in malonaldehyde derivatives: Substituent effects and *quasi*-aromaticity of the proton bridge

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## Abstract

The proton transfer in malonaldehyde and in some of its derivatives have been considered in order to study the interrelation between the reaction barrier and the  $\pi$ -delocalization in the *quasi*-ring. A set of simple and mostly common substituents having different properties in resonance effect according to values of substituents constants were chosen in order to simulate the influence of substitution in position 2 or in position 1 (or 3) of malonaldehyde on the *quasi*-aromaticity and H-bonding. The following substituents have been taken into consideration: NO, NO<sub>2</sub>, CN, CHO, F, H, CH<sub>3</sub>, OCH<sub>3</sub>, OH, and NH<sub>2</sub>. Our results show that when the substituent is attached at position 2 of the *quasi*-ring, the resonance effect predominates over the field/inductive effect which leads to changes in H-bonding and *quasi*-aromaticity of the ring motif, while in the case of 1(3) substitution the field/inductive effect is significantly more effective influencing the HB strength, and thus, the proton transfer barrier. Somehow counterintuitively, for the 1(3) substituted systems, the most stable isomer is the one having the weakest HB and lower aromaticity. The reason for this surprising behaviour is discussed.

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**Keywords:** Malonaldehyde derivatives; Resonance-assisted hydrogen bonds (RAHB); Local aromaticity; *para*-Delocalization index (PDI); Harmonic oscillator model of aromaticity index (HOMA); Six-centre indexes (SCI)

## 1. Introduction

The investigations on the hydrogen bond (HB) occupy one of the most important places in such branches of sciences as chemistry, biochemistry or physical biology. This arises from the fact that the HB plays a crucial role in many chemical and biological processes [1,2]. This interaction is also mostly responsible for the arrangement of molecules in many crystals [3,4]. Thus, the HB is one of the most important aspects in supramolecular chemistry and molecular engineering [5]. In general the very exceptional properties of H-bonding arise from two facts; firstly, the HB is significantly directional, since the arrangement of atoms

within the H-bridge is most favourable for linear geometry, and secondly, the HB is strong enough to assemble molecular systems in aggregates, but weak enough to be disrupted in conditions such as those occurring in living organisms. The strongest known HBs are those assisted by additional effects, e.g. charge-assisted hydrogen bonds (CAHB) in which the binding energy is increased by the additional charge distribution favourable for H-bonding formation [6,7], or resonance-assisted hydrogen bonds (RAHB) which have been thoroughly described, systematized, and analyzed by Gilli and co-workers in their numerous studies [6,8–14]. According to Gilli's concept of RAHB the additional effect of stabilization is connected with the partial delocalization of  $\pi$ -electrons within the HB motif (usually ring or chain) containing conjugated formally single and double bonds (see Chart 1). Indeed, Bickelhaupt et al. [15,16] have recently proved in DNA base pairs connected through RAHB that it is the relaxation in the  $\pi$ -system that provides the additional stabilization in RAHB,

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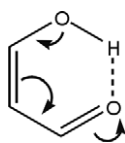


Chart 1.

the  $\sigma$ -electron system being hardly affected by these  $\pi$ -reorganization. This  $\pi$ -electron effect leads to the elongation of formally double and shortening of formally single bonds. Additionally, the elongation of the proton-donating bond and the shortening of the proton-acceptor distance is observed [17]. It is possible to consider this kind of interaction as a first stage of the proton transfer reaction, which in its final result could lead to the reorganization of bond ordering within the given HB motif. Thus, for a given motif there are two H-bonded forms corresponding to the two possible tautomeric isomers.

The cyclic enolic RAHB structure depicted in Chart 1 contains six delocalized electrons that readily suggest the formation of a pseudoaromatic or *quasi*-aromatic ring [18–20]. The relation between HB strength and the  $\pi$ -electron delocalization in the pseudoaromatic ring has been the focus of different studies [12,20,21] (for a recent review see Ref. [22]). In most of these studies, the RAHB is fused to an aromatic ring and the change of aromaticity undergone by this aromatic system upon RAHB formation has been also the subject of several recent works [20–24]. The authors of these studies have found that, in many cases, the RAHB affects dramatically the  $\pi$ -electron delocalization in the fused aromatic rings. Similarly, different aromatic rings attached to the  $\pi$ -system of the pseudoaromatic ring in RAHBs have a large influence on the strength of the RAHB [23]. However, in other cases as for instance, in the tautomerization reaction of 2-hydroxybenzoyl derivatives, aromaticity seems to play only a minor role. In this latter case, it has been found that the approach between the oxygen atoms that yields the internal HB, which occurs in the midpoint of the proton transfer, depends on the acid/base characteristics of the proton donor and acceptor groups and it is not substantially affected by the aromaticity of the whole system [25]. It should be mentioned however, that the  $\pi$ -electron delocalization proceeding within the systems investigated in that study should be substantially restricted by the stability of the aromatic benzene ring. Such interrelations between aromaticity and H-bonding in systems with RAHBs has been clearly demonstrated and thoroughly characterized [23,24]. It is worth to point out that, in general, in the proton-transfer-generated-tautomerization, the  $\pi$ -electron delocalization plays a significant role [26]. On the other hand, it has been recently reported that the delocalization within RAHB motif not always must be accompanied by the strengthening of the HB. It has been shown that external factors may lead to additional delocalization which is accompanied by the weakening of the H-bonding [27,28]. This conclusion is in agreement with recent discussions

about the interrelation between HB strength and resonance-assisted stabilization [29–31].

As said before, in a previous study [23], we have analyzed the interrelation between the RAHB formation and the changes in the aromaticity of adjacent aromatic rings. In the present work, we concentrate our efforts in the analysis of the aromaticity of the *pseudo*-ring in the archetypal and one of the simplest RAHB, i.e., that occurring in malonaldehyde. The six-membered ring (6-MR) of malonaldehyde can not be considered fully aromatic since it does not fulfill the basic criteria of the aromatic compounds (e.g. Hückel rule) [32]. However, since it is a 6-MR motif in which partial  $\pi$ -electron delocalization occurs, it can be considered as a *quasi*-aromatic system [33–36]. In fact, it is possible to state that the malonaldehyde and related systems manifest some characteristics similar to these of typically aromatic systems, e.g., partial  $\pi$ -electron delocalization, partial equalization of bond lengths, planarity, and finally additional energetic stability, since formation of the HB and in this way formation of the *quasi*-ring leads to an energetically more stable form of malonaldehyde. What is more, the *quasi*-aromaticity can be numerically evaluated with some of the descriptors which were originally designed for typically aromatic systems. Therefore, a set of aromaticity indices can be used in order to quantify the aromatic, or more precisely *quasi*-aromatic character of the system under consideration. Using these tools we analyze in the present work the interplay between  $\pi$ -electron delocalization within the extra *quasi*-ring formed by the H-bridge and the characteristic of proton transfer reaction by introducing perturbations in the ring in the form of different substituents located at positions 2 and 1(3) of the ring. Both tautomeric forms as well as the transition state corresponding to the proton transfer reaction leading to tautomerization are investigated. In order to diversify the set of analyzed systems we have considered substituents attached to the *quasi*-aromatic ring with different electron-donating/accepting properties. Substituent constants have been used in order to quantify the substituent effect [37].

## 2. Methodology

Geometries of all molecular systems were optimized without any restraints using DFT-B3LYP functional [38–40] in conjunction with the 6-311++G(d,p) basis set implemented in the GAUSSIAN 03 set of codes [41]. As it has been recently shown on the basis of calculations performed for a series of modelled DNA base pairs, this level of functional density theory gives satisfactory results for H-bonded systems [42]. Frequency calculations have been performed at the same level of approximation. All systems correspond to energy minima and no imaginary frequencies were observed for ground state systems, while for transition state systems there were single imaginary frequencies corresponding to the proton transfer (PT) reaction. Calculations refer in all cases to the most stable conformer of all malonaldehyde derivative isomers.

As a geometrical indicator of a local aromaticity, the geometry-based HOMA index has been applied. According to its definition [43,44] HOMA can be expressed by the following equation:

$$\text{HOMA} = 1 - \frac{1}{n} \sum_{j=1}^n \alpha_i (R_{\text{opt},i} - R_j)^2 \quad (1)$$

where  $n$  represents the total number of bonds in the molecule and  $\alpha_i$  is a normalization constant (for C–C and C–O bonds:  $R_{\text{opt,CC}} = 1.388 \text{ \AA}$ ,  $R_{\text{opt,CO}} = 1.265 \text{ \AA}$ ,  $\alpha_{\text{C-C}} = 257.7$ , and  $\alpha_{\text{C-O}} = 157.38$ ) fixed to give HOMA = 0 for a model nonaromatic system, e.g., the Kekulé structure of benzene and HOMA = 1 for the system with all bonds equal to the optimal value  $R_{\text{opt},i}$ , assumed to be realized for fully aromatic systems [45]. The higher is the HOMA value, the more “aromatic” is the ring in question and, hence, the more delocalized  $\pi$ -electrons of the system.

Different aromaticity criteria based on electron delocalization measures have been employed [46,47]. These indexes try to measure the cyclic electron delocalization of mobile electrons in aromatic rings. First, the *para*-delocalization index (PDI) [48], which is an average of all delocalization indexes (DI) [49,50] of *para*-related carbon atoms in a given 6-MR. The DI value between atoms  $A$  and  $B$ ,  $\delta(A, B)$ , is obtained by double integration of the exchange-correlation density ( $\Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2)$ ) over the space occupied by atoms  $A$  and  $B$ :

$$\delta(A, B) = -2 \int_A \int_B \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2. \quad (2)$$

For monodeterminantal closed-shell wavefunctions one obtains

$$\delta(A, B) = 4 \sum_{i,j}^{N/2} S_{ij}(A) S_{ij}(B). \quad (3)$$

The summations in Eq. (3) run over all the  $N/2$  occupied molecular orbitals.  $S_{ij}(A)$  is the overlap between molecular orbitals  $i$  and  $j$  within the basin of atom  $A$ . It should be pointed out that no direct usage of the Atoms in Molecules (AIM) theory of Bader [51,52] has been applied in this work, except for the fact that we make the use of AIM atomic partition defined from the condition of zero-flux gradient in the one-electron density [51,52],  $\rho(\mathbf{r})$ , to compute  $S_{ij}(A)$  values. However, as shown before [46,53,54], other partitions of the molecular space could also be used.  $\delta(A, B)$  provides a quantitative idea of the number of electron pairs delocalized or shared between atoms  $A$  and  $B$ . Therefore, the PDI is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Previous works [48,55] have shown that for a series of planar and curved polycyclic aromatic hydrocarbons there is a satisfactory correlation between NICS, HOMA, and PDI.

Second, multicenter indexes recently defined by Giambiagi and co-workers. For a closed-shell monodeterminantal wavefunction of a 6-MR molecule Giambiagi's proposal of aromaticity index reads [56]

$$\text{KSCI} = 24 \sum_{i,j,k,l,m,n} S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{lm}(D) S_{mn}(E) S_{ni}(F). \quad (4)$$

A particular extension of the latter index have been devised by Bultinck, Ponec, and co-workers [57]. According to these authors summing up all the KSCI resulting from the permutations of indexes  $A, B, \dots, F$  defines a new index of aromaticity, in the case of a 6-MR, the so-called six-centre index (SCI) [57]. The particular expression of SCI for a decomposition of the molecular space into atomic basins, in the case of a monodeterminantal closed-shell wavefunction, reads as follows:

$$\text{SCI} = \frac{16}{3} \sum_{\alpha} \sum_{i,j,k,l,m,n} \Gamma_{\alpha} [S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{lm}(D) \times S_{mn}(E) S_{ni}(F)], \quad (5)$$

where  $\Gamma_{\alpha}$  stands for a permutation operator which interchanges the atomic labels  $A, B, \dots, F$  to generate up to 6! combinations. Generally the values of SCI and KSCI are in tight correlation because the dominant contribution to SCI is the Kekulé structure, nonetheless some exceptions may arise.

Different, experimentally estimated substituent constants have been taken into account in order to investigate the substituent effect in substituted malonaldehyde, among them,  $\sigma^+$ ,  $\sigma^-$ ,  $F$ ,  $R^+$  and  $R^-$  [37]. These substituent constants are numerically characterizing mutual electron interaction between a given substituent and the *para*-placed reactivity centre proceeding through the aromatic ring.

The  $\sigma^+$  is the substituent constant originally estimated from solvolysis of dimethylphenylcarbinyl chloride derivatives in which the *para* placed (with respect to a given substituent, see Chart 2, where X is the reactivity centre and R is the considered substituent) reactivity centre, i.e.  $\text{C}(\text{CH}_3)_2\text{Cl}$ , could effectively delocalize a positive charge [58]. In other words,  $\sigma^+$  values are estimated for centre which introduces positive charge onto its carrier ring. Values of  $\sigma^-$  were originally estimated from pK values of *para*-substituted phenols and anilines. In other words, these values have been estimated for the centre having lone electron pairs, e.g. OH or  $\text{NH}_2$  group, so the centre which introduces negative charge onto its carrier ring [59].  $F$  values reflect field/inductive properties of a given substituent, while  $R^+$  and  $R^-$  are the resonance constants obtained for suitable centres of reactivity. A large positive value of



Chart 2.

Table 1  
Substituent constants corresponding to the substituents considered in this work

Substituent	$\sigma^+$	$\sigma^-$	$F$	$R^+$	$R^-$
OH	-0.920	-0.370	0.330	-1.250	-0.700
OCH <sub>3</sub>	-0.780	-0.260	0.290	-1.070	-0.550
CH <sub>3</sub>	-0.310	-0.170	0.010	-0.320	-0.180
NH <sub>2</sub>	-1.300	-0.150	0.080	-1.380	-0.230
F	-0.070	-0.030	0.450	-0.520	-0.480
H	0.000	0.000	0.000	0.000	0.000
CN	0.660	1.000	0.510	0.150	0.490
CHO	0.730	1.030	0.330	0.400	0.700
NO <sub>2</sub>	0.790	1.270	0.650	0.140	0.620
NO	-	1.630	0.490	-	1.140
Li	-	-	-	-	-

a given constant implies high electron-withdrawing power by inductive and/or resonance effect, relative to the hydrogen atom; a large negative value of a given constant implies high electron-donating power relative to the hydrogen atom. The values of the  $\sigma^+$ ,  $\sigma^-$ ,  $F$ ,  $R^+$ , and  $R^-$  substituent constants for the substituent studied in this work have been collected in Table 1.

### 3. Results and discussion

We have divided this section into two subsections. In the first one, we discuss the systems substituted at position 2 in malonaldehyde, while the second one is devoted to analysis of the substituent effect when the substitution takes place at position 1(3).

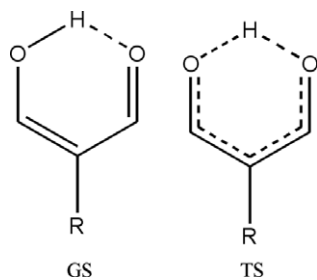


Chart 3.

Table 2  
Selected energetic, geometrical and topological parameters of malonaldehyde derivatives substituted at position 2

Substituent	$\Delta E^\ddagger$	$d(\text{O}\cdots\text{O})_{\text{GS}}$	$d(\text{H}\cdots\text{O})_{\text{GS}}$	$d(\text{O}-\text{H})_{\text{GS}}$	$d(\text{O}\cdots\text{O})_{\text{TS}}$	$\delta(\text{O}-\text{H})_{\text{GS}}$	$\delta(\text{O}-\text{H})_{\text{TS}}$	$\delta(\text{O}\cdots\text{H})_{\text{GS}}$	$\delta(\text{O}\cdots\text{H})_{\text{TS}}$
OH	3.70	2.605	1.730	0.993	2.366	0.501	0.311	0.107	0.311
OCH <sub>3</sub>	5.08	2.611	1.730	0.993	2.361	0.495	0.293	0.113	0.327
CH <sub>3</sub>	3.48	2.573	1.689	0.995	2.360	0.486	0.308	0.122	0.314
NH <sub>2</sub>	2.91	2.569	1.677	0.999	2.364	0.480	0.315	0.125	0.307
F	4.15	2.632	1.766	0.990	2.369	0.502	0.311	0.106	0.311
H	3.20	2.584	1.695	0.998	2.366	0.486	0.311	0.121	0.311
CN	2.83	2.562	1.671	1.001	2.363	0.472	0.308	0.125	0.308
CHO	2.87	2.563	1.668	1.003	2.368	0.473	0.315	0.128	0.305
NO <sub>2</sub>	2.65	2.558	1.663	1.004	2.368	0.467	0.309	0.127	0.309
NO	3.28	2.581	1.692	1.001	2.373	0.474	0.318	0.121	0.298
Li	2.91	2.551	1.653	0.998	2.357	0.482	0.312	0.131	0.312

Delocalization indexes,  $\delta$ , in a.u.,  $\Delta E^\ddagger$  in kcal/mol, distances in Å.

#### 3.1. Part 1: systems substituted at position 2 of malonaldehyde

For these systems, we have symmetric energy profiles in which the reactants (GS) are connected through a PT transition state (TS) to products with the same structure as reactants (see Chart 3). For these systems, the TS is the most symmetric species and, therefore, the aromaticity of the TS is expected to be the largest along the reaction coordinate.

Table 2 lists the energy differences between TS and GS,  $\Delta E^\ddagger$ , which corresponds to the energy barrier of the PT reaction, as well as selected geometrical and electronic parameters of the H-bridge. Values of aromaticity indices estimated for the *quasi*-ring formed by H-bonding interaction are collected in Table 3. As it can be seen from the data collected, all values of  $\Delta E^\ddagger$  are in the range of 2.7–5.1 kcal/mol and therefore it is possible to qualify these HBs as low barrier double well HBs [60]. It should be pointed out, that as compared to the unsubstituted system all changes observed for parameters collected derive directly from the influence of the substituent R onto the electronic structure of malonaldehyde moiety (see Chart 3). This influence proceeds in two possible manners; first, there is a mesomeric effect in which the substituent is potentially involved in  $\pi$ -electron communication with the malonaldehyde moiety, and second, there is a field/inductive effect, which mainly concerns the substituted C atom of malonaldehyde. In the latter case, the electronic effect depends primarily on the electronegativity of the group attached to the *quasi*-ring. It can be stated that the field/inductive effect is in general weak in the case of substituents such as CH<sub>3</sub>. This is reflected with relatively small values of the corresponding substituent constant  $F$ . The rest of substituents reflect diverse possibilities of influencing the malonaldehyde group, but in general all these substituents can be treated as electron-withdrawing ones (by means of field/inductive effect) with positive values of  $F$  constant. The only exception is the case of the lithium substituent, which should be considered as electron-donating species. Unfortunately, for this substituent the values of

Table 3

Values of indexes of aromaticity estimated for the *quasi*-ring of malonaldehyde derivatives substituted at position 2

Substituent	HOMA <sub>GS</sub>	HOMA <sub>TS</sub>	ΔHOMA	PDI <sub>GS</sub>	PDI <sub>TS</sub>	ΔPDI	KSCI <sub>GS</sub>	KSCI <sub>TS</sub>	ΔKSCI	SCI <sub>GS</sub>	SCI <sub>TS</sub>	ΔSCI
OH	0.595	0.967	0.373	0.044	0.054	0.010	3.59	7.00	3.41	12.30	24.56	12.26
OCH <sub>3</sub>	0.592	0.955	0.363	0.044	0.059	0.015	3.54	6.70	3.16	12.13	23.96	11.83
CH <sub>3</sub>	0.593	0.957	0.364	0.045	0.055	0.009	3.80	7.10	3.30	12.44	23.87	11.43
NH <sub>2</sub>	0.588	0.952	0.364	0.043	0.052	0.008	3.90	7.00	3.10	12.84	23.86	11.02
F	0.602	0.982	0.380	0.045	0.055	0.011	3.40	6.90	3.50	11.85	24.99	13.14
H	0.659	0.972	0.312	0.044	0.052	0.008	3.88	7.10	3.22	12.90	24.07	11.17
CN	0.588	0.917	0.328	0.037	0.044	0.007	3.60	6.50	2.90	12.18	21.75	9.57
CHO	0.600	0.929	0.329	0.034	0.041	0.007	3.59	6.50	2.91	11.67	20.94	9.27
NO <sub>2</sub>	0.659	0.948	0.289	0.034	0.039	0.006	3.50	6.30	2.80	12.00	21.20	9.20
NO	0.606	0.913	0.307	0.030	0.037	0.007	3.14	5.82	2.68	10.48	19.33	8.85
Li	0.529	0.885	0.356	0.049	0.057	0.008	4.26	7.40	3.14	12.93	23.36	10.43

PDI in a.u., SCI and KSCI in 10<sup>-4</sup> a.u.

substituent constants are not available in the literature. As it has been mentioned, the field/inductive effect mainly influences the substituted carbon atom and, in general, we expect that this effect will be only slightly influencing the *quasi*-aromaticity and H-bonding in the *quasi*-ring. In the case of mesomeric (resonance) effect, the situation is more complicated, since in this case the inner, resonance effect within the *quasi*-ring has to be additionally considered. Therefore, it is worth to take a closer look into the resonance structures of substituted malonaldehyde system. In Fig. 1, the resonance effect proceeding in this system has been divided into three separated model situations illustrating three mesomeric effects which are cooperating or competing between each other.

The first one is a resonance effect taking place within the *quasi*-ring of malonaldehyde moiety (**1a** ↔ **1b**). In this case,

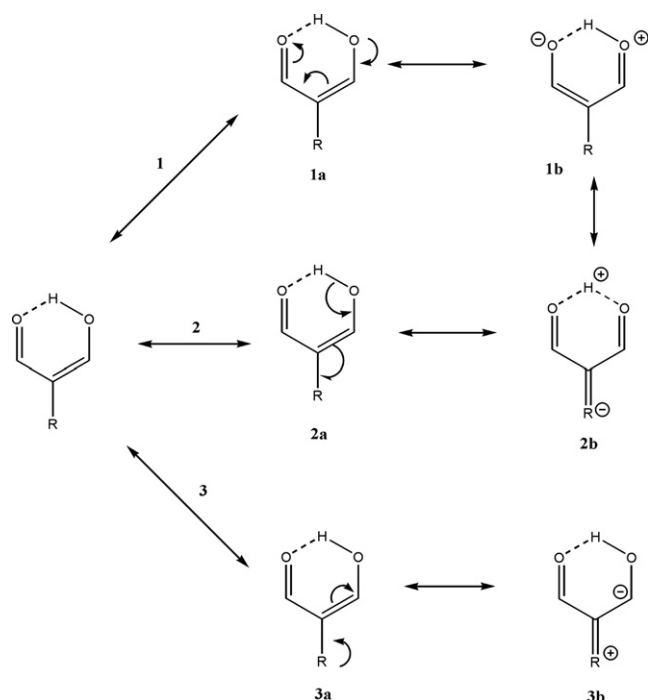


Fig. 1. Schematic representation of resonance (mesomeric) effect in malonaldehyde systems substituted at position 2.

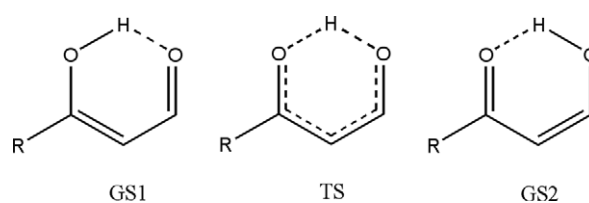


Chart 4.

the substituent does not participate in  $\pi$ -electron delocalization and the effect proceeds apart from the character of attached substituent. This is the fully illustrated case of unsubstituted malonaldehyde ( $R = H$ ). This effect leads to partial delocalization of  $\pi$ -bonds and in this way favours H-bonding. Additionally it decreases the energetic barrier of PT reaction (the stronger HB, the more equalized the O–H and H $\cdots$ O bond lengths are, and therefore, the closer the geometry of the GS system to that of the TS is). Thanks to this effect, the intramolecular H-bridge in malonaldehyde is usually considered as a resonance-assisted HB (RAHB).

The second case corresponds to the situation in which the substituent attached to malonaldehyde has electron-withdrawing properties (by means of mesomeric effect) and is participating in electron delocalization within the whole system. It is possible to postulate, that both effects **1** and **2** are cooperating each other (there is a direct transition between canonical structures of effects **1** and **2**), that result in a stronger HB. In fact, for all GS systems with electron-withdrawing substituents (positive  $R$  values),  $d(O-H)_{GS}$  is larger and the  $d(O\cdots H)_{GS}$  shorter thus indicating a stronger HB and an advancement of the PT process. The same trend is seen in the corresponding  $\delta(O-H)_{GS}$  and  $\delta(O\cdots H)_{GS}$  delocalization indices. Because of the more advanced PT, for most systems with electron-withdrawing substituents the value of  $\Delta E^\ddagger$  is smaller than the corresponding value estimated for unsubstituted malonaldehyde. On the other hand, the molecular structure of the TS is quite independent of the substituent as can be seen in the  $d(O\cdots O)_{TS}$  values (and also in the  $d(O-H)_{TS}$  distances not given in Table 2) along the series. With respect to the aromaticity of the *quasi*-ring, the participa-

tion of the resonance structure **2b** in Fig. 1, should lead to a decrease of the delocalization and *quasi*-aromatic character of the malonaldehyde *quasi*-ring in both the GS and TS. This is reflected by the corresponding values of aromaticity indices in Table 3, with the exception of the Li system for some of the indices. Additionally, the change of aromaticity from GS to TS is smaller in this case, which can be explained by taking into account that the PT in the GS is already quite advanced, and the geometrical changes from GS to TS are comparatively smaller.

In the third case of electron-donating substituents (structures **3a** and **3b** in Fig. 1), the effect of resonance in the HB is strongly limited. The only possible effect is the introduction of partial negative charge into one of the carbon atoms. So in this case the influence of substituents on delocalization of electrons is reduced. Indeed, the participation of structure **3b** weakens the HB, since the negative charge formally located on the C atom should block the PT. Thus the participation of structure **3b** leads to an increase of the energy barrier of the PT as compared to unsubstituted systems with the only exception of NH<sub>2</sub>, although, for this latter substituent, it was observed in a previous work that the  $\pi$ -electron donation can be partially inhibited by the  $\sigma$ -electron accepting character of the N atom [61]. The weakening of the HB for the rest of electron-donating substituents can be corroborated from the  $d(\text{O}-\text{H})_{\text{GS}}$ ,  $d(\text{O}\cdots\text{H})_{\text{GS}}$ , and  $\Delta E^\ddagger$  values collected in Table 2. On the other hand, the influence of the substituent on the aromaticity of the *quasi*-ring is now smaller as deduced from the values of the aromaticity indices for the substituted systems when compared to those for the unsubstituted malonaldehyde (see Table 3).

It is well known, that the geometrical parameters of the HB reflect the strength of this bond. Usually, the shorter the (D)H $\cdots$ A distance is, the stronger the HB. In the case of O-H $\cdots$ O bonds this is additionally accompanied by the lengthening of O-H bond and by shortening of O $\cdots$ O distance [17,22]. As it can be seen in the attached Fig. 2, there are clear relations between the magnitude of PT reaction barrier ( $\Delta E^\ddagger$ ) and the geometric parameters of the H-bridge. Similarly, it is possible to find such relations for delocalization indices estimated for suitable bonds in the H-bridge and  $\Delta E^\ddagger$ . Clearly, the stronger the HB is, the lower the energetic barrier for the PT is. This is in agreement with the Lefler–Hammond postulate according to which systems of stronger HBs are structurally closer to TSs and consequently they have lower  $\Delta E^\ddagger$  values [62,63]. Interestingly, it is not possible to observe any relations between  $\Delta E^\ddagger$  and distances or delocalization indices within H-bridges corresponding to TS geometries.

Summarizing, we have shown that, in the case of the analyzed set of systems substituted at position 2, the interaction between substituents and *quasi*-ring is proceeding mainly through the resonance effect favouring the PT in the case of electron-withdrawing substituents and disfavoring it for electron-donating groups.

One of the main aims of this work is to find if there is some relation between the PT barrier and the *quasi*-aromatic character of the investigated systems. The most evident fact is that all aromaticity indices reflect the larger aromatic character of the TS when compared to that of the corresponding GS. Therefore, the process of intramolecular PT in malonaldehyde molecule is evidently accompanied by delocalization of electrons within the extra ring

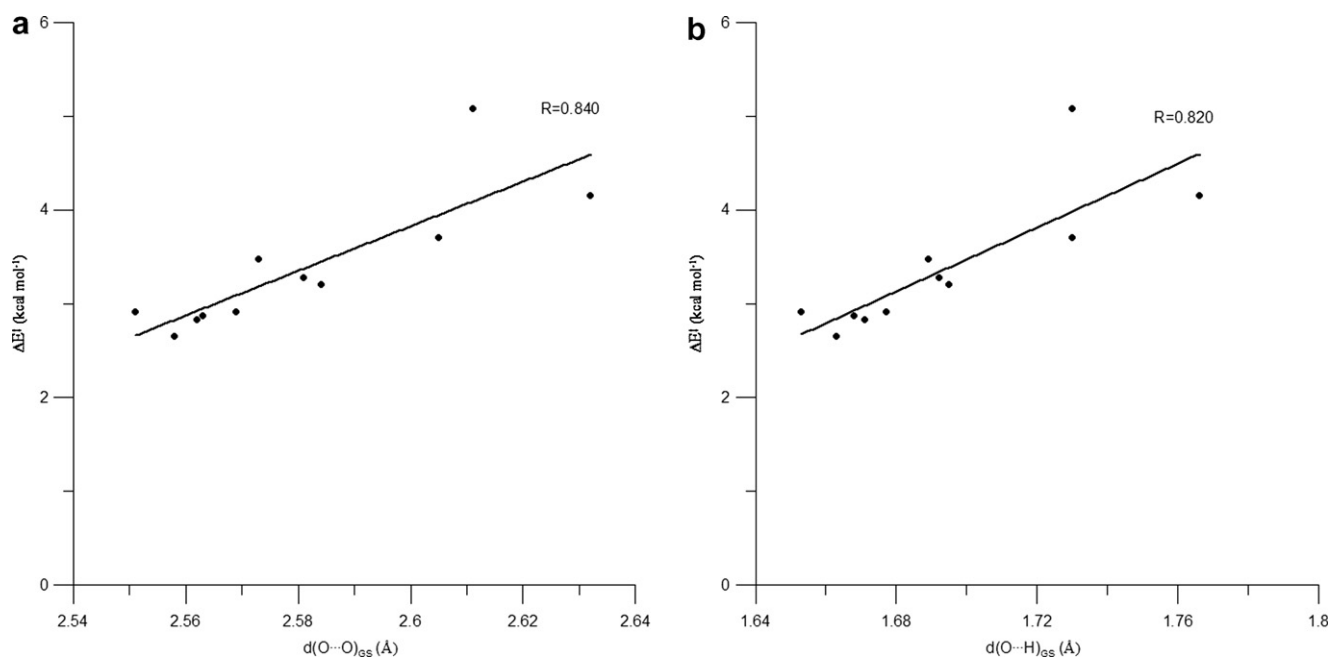


Fig. 2. Interdependences between  $\Delta E^\ddagger$  and geometrical parameters of H-bridge. All data correspond to GS geometries: (a)  $\Delta E^\ddagger$  vs.  $d(\text{O}\cdots\text{O})$ , (b)  $\Delta E^\ddagger$  vs.  $d(\text{O}-\text{H})$ .

formed by H-bonding. This situation is comparable to that found in the Li-bonded derivatives of malonaldehyde, in which  $H^+$  is replaced by  $Li^+$ . In those systems,  $Li^+$  is located alike  $H^+$  in our TS species, which seems to lead to increase of electron delocalization within the *quasi*-ring if comparing with H-bonded analogues [64]. There is a lack of interdependences between  $\Delta E^\ddagger$  and absolute values of aromaticity indices, both considering GSs and TSs. This is directly connected with differences in  $\pi$ -electron communication between given substituents and  $\pi$ -electronic system of the *quasi*-ring. However, there are some close to linear relations between  $\Delta E^\ddagger$  and changes of aromaticity measured as difference between values of aromaticity indices estimated for GS and its corresponding TS. Interestingly, it seems that relative increase of aromaticity when going from GS to TS is greater in the case of systems having greater value of  $\Delta E^\ddagger$ . It can be explained with the fact that stronger GS HBs are those which are closer energetically and geometrically to the TS. Therefore, for the systems with stronger HBs the change of aromaticity due to formation of TS from relatively more *quasi*-aromatic GS is smaller. The smaller  $\Delta E^\ddagger$  value observed for systems with stronger HBs is obviously in agreement with the above-mentioned Leffler–Hammond postulate. Some of the relations discussed in this paragraph are graphically represented in Fig. 3.

The effect of substitution can be quantified by the use of substituent constants estimated for suitable chemical groups. Table S1 of the Supporting material collects the correlation coefficients corresponding to linear regressions estimated for dependences between substituent constants and selected parameters of systems under discussion. As it can be seen, the only satisfactory relations can be found for  $R^-$ . There are also some relatively good relations for

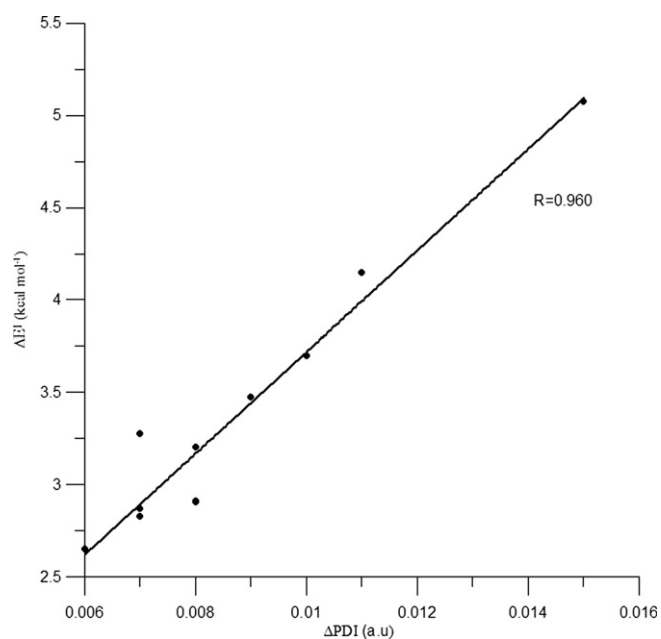


Fig. 3. Interdependences between  $\Delta E^\ddagger$  and  $\Delta PDI$ .

$\sigma^-$ , however it is hard to find satisfactory values for the rest of substituent constants. It can be interpreted in following way: (1) the H atom in *quasi*-ring adopts a behaviour similar to that of the reactivity centre which can introduce a negative charge onto its carrier ring (see the definition of substituent constants used in this work). This conclusion should not be surprising, since H atom relatively easily shares its electronic charge and in this way adopts positive charge; and (2) the main influence of substituents proceeds through the resonance effect, since there are good relations for  $R^-$ , worse relations for  $\sigma^-$  and practically complete lack of relations for  $F$ .

### 3.2. Part 2: systems substituted at position 1 (or 3)

Systems substituted at position 1(3) have nonsymmetric energy profiles in which the reactants (GS1) are connected through a TS to products (GS2) (see Chart 4). In the case of 1(3) substitution GS1 systems with both  $-Li$  and  $-OCH_3$  substituents are unstable, and therefore were excluded from the discussion.

Tables 4 and 5 collect selected parameters of systems under discussion. The data for  $R = H$  has been already provided in Tables 2 and 3. First of all, it can be rapidly noticed that GS2 is more stable than GS1 (except for  $R = CH_3$  that has almost degenerated GS1 and GS2 species), although GS1 presents a stronger HB than GS2. From Table 4 it can be observed that GS1 in substituted malonaldehydes have shorter  $O \cdots H$  distances than GS2 as well as higher  $\delta(O \cdots H)$ , which indicate a stronger HB. In addition, according to Table 5 aromaticity indices, the *quasi*-rings in GS1 are, in general, more aromatic. Thus, despite GS1 has a stronger HB and a more aromatic *quasi*-ring, it is less stable than GS2. The reason for the higher stability of GS2 is, in our opinion, twofold: (1) GS1 and GS2 are systems with  $4\pi$ -electrons and such antiaromatic species prefer a localized situation; and (2) substituents with positive  $F$  values (all analyzed substituents have  $F > 0$ ) stabilize GS2 and destabilize GS1 due to the inductive/field effect. Counterintuitively, substituents with  $F > 0$  stabilize GS2 and destabilize GS1 while at the same time favours H-bonding in GS1 and disfavours it in GS2. Therefore, in these systems we have the amazing situation that species with stronger HBs and higher aromaticity are the less stable.

Fig. 4 depicts possible ways through which the resonance effect can proceed in the analyzed systems. In this kind of substitution it is necessary to differentiate the substitution in GS1 and GS2. It can be seen in Fig. 4, that both in the case of GS1 as well as GS2 system the electron-withdrawing substituents are weakening the possibilities of HB formation (see structures 1b and 3b). On the contrary, in the case of electron-donating substituent (see structures 2b and 4b) the resonance effect is favouring H-bonding. Moreover, in systems substituted at position 1(3), the substituent is located near the H-bridge and the influence of the field/inductive effect is more important than in systems



Table 4  
Selected energetic and geometrical and topological parameters of malonaldehyde derivatives substituted at position 1(3)

Substituent	$\Delta E_{GS}$	$\Delta E_1^\ddagger = E_{TS} - E_{GS1}$	$\Delta E_2^\ddagger = E_{TS} - E_{GS2}$	GS1				GS2				TS				
				$d(O \cdots O)$	$d(H \cdots O)$	$d(O-H)$	$\delta(O-H)$	$\delta(O \cdots H)$	$d(O \cdots O)$	$d(H \cdots O)$	$d(O-H)$	$\delta(O-H)$	$d(O \cdots H)$	$d(O \cdots O)$	$\delta(O \cdots H)$	$\delta_1(O \cdots H)$
OH	7.81	0.00	7.81	2.430	1.429	1.066	0.397	0.208	2.635	1.775	0.988	0.510	0.101	2.419	0.389	0.217
F	9.42	0.05	9.47	2.472	1.510	1.041	0.420	0.179	2.677	1.837	0.984	0.525	0.088	2.412	0.382	0.226
NH <sub>2</sub>	4.58	0.36	4.94	2.480	1.518	1.033	0.425	0.175	2.587	1.701	0.996	0.489	0.119	2.383	0.352	0.266
CH <sub>3</sub>	-0.12	2.85	2.73	2.560	1.653	1.001	0.473	0.132	2.571	1.681	0.998	0.482	0.124	2.364	0.307	0.314
CN	1.21	2.80	4.00	2.576	1.685	0.999	0.474	0.122	2.604	1.732	0.993	0.492	0.110	2.365	0.314	0.302
NO <sub>2</sub>	6.81	1.13	7.94	2.545	1.642	1.009	0.455	0.134	2.677	1.843	0.983	0.523	0.085	2.377	0.346	0.266
CHO	0.44	3.19	3.63	2.585	1.703	0.996	0.481	0.117	2.599	1.722	0.994	0.489	0.113	2.364	0.312	0.307
NO	2.62	2.64	5.26	2.585	1.704	0.997	0.480	0.118	2.637	1.779	0.988	0.507	0.101	2.367	0.325	0.294

Delocalization indexes,  $\delta$ , in a.u.,  $\Delta E^\ddagger$  in kcal/mol, distances in Å.

substituted in position 2. As said before, substituents with positive  $F$  values stabilize H-bridge in GS1 and destabilize it in GS2. Thus, because of more favourable field/inductive effects, we expect stronger HBs in GS1 than in GS2. This is confirmed by both the geometrical and energetic parameters collected in Table 4. These observations indicate also on relatively significant role of field/inductive effect in the case of 1(3) substitution.

From a geometrical point of view, differences in H-bridge parameters for the different substituents estimated for GS2 are relatively small if comparing with the related values in GS1. The largest difference between H $\cdots$ O distances are 0.162 Å for GS2, while in the case of GS1 it amounts 0.275 Å. Therefore in GS1 the influence of substitution on the H-bridge is significantly more effective when comparing with GS2. As it was pointed out before, distances within H-bridge of GS1 are systematically shorter than in the case of GS2, indicating stronger H-bonding in GS1. This is particularly true in the case of electron-donating substituent in which the contribution of structure **2b** of Fig. 4 should favour formation of H-bonding. Therefore, the more electron-donating substituent (by means of resonance effect) attached to the GS1, the stronger should be the HB. For electron-withdrawing substituents the HB is weakened because structure **1b** does not contribute to stabilize HB formation. In fact, as it can be seen in Table 4, the shortest distances in the H-bridge of GS1 are observed for electron-donating substituents (OH, F, NH<sub>2</sub>) while for electron-withdrawing groups the distances in H-bridge are relatively longer indicating weaker H-bonding. Similar conclusions can be made on the basis of electron delocalization indices estimated for suitable bonds in H-bridge. For GS2, the resonance and the field/inductive effects on HB formation counteract in electron-donating groups (with  $R < 0$  and  $F > 0$ ) and they go in the same direction (disfavouring H-bonding as compared to unsubstituted malonaldehyde) for electron-withdrawing groups (with  $R > 0$  and  $F > 0$ ). As a result, in all cases, except  $R = \text{CH}_3$ , the HB is longer in substituted than in the unsubstituted system.

From an energetic point of view, the set of investigated systems can be divided into two subgroups. In one group we have the systems with  $\Delta E_{GS}$  close to zero. These are all species with substituents attached by a carbon atom to the *quasi*-ring ( $R = \text{CH}_3$ , CN, and CHO). In these cases, the difference between the total energy of both GSs and TS is relatively small. The barrier of PT is relatively low for these systems, and both GS systems are almost isoenergetic. In the next group, formed by substituents for which the atom directly attached to its carrier ring is not a carbon atom,  $\Delta E_{GS}$  adopts relatively greater magnitude. In all these cases GS2 is clearly more stable than GS1. It seems, therefore, that the character of the R-C<sub>carbonyl</sub> bond (ionic/covalent or polarised/not polarised) determine the stability of GS1 system. If there is attached to a carbon atom, so when the suitable C-R bond is weakly polarised, then GS1 and GS2 are almost degenerated. If the attached atom

Table 5

Values of indexes of aromaticity estimated for the *quasi*-ring of malonaldehyde derivatives substituted at position 1(3)

Substituent	HOMA <sub>GS1</sub>	HOMA <sub>GS2</sub>	HOMA <sub>TS</sub>	$\Delta$ HOMA <sub>1</sub>	$\Delta$ HOMA <sub>2</sub>	PDI <sub>GS1</sub>	PDI <sub>GS2</sub>	PDI <sub>TS</sub>	$\Delta$ PDI <sub>1</sub>	$\Delta$ PDI <sub>2</sub>
OH	0.912	0.529	0.924	0.012	0.395	0.039	0.032	0.039	0.000	0.007
F	0.860	0.518	0.938	0.078	0.419	0.042	0.036	0.044	0.002	0.008
NH <sub>2</sub>	0.865	0.446	0.918	0.054	0.472	0.034	0.028	0.035	0.001	0.007
CH <sub>3</sub>	0.694	0.562	0.948	0.254	0.386	0.042	0.039	0.048	0.006	0.009
CN	0.596	0.704	0.960	0.365	0.256	0.040	0.043	0.050	0.009	0.006
NO <sub>2</sub>	0.639	0.630	0.630	-0.010	0.000	0.043	0.044	0.051	0.008	0.007
CHO	0.587	0.707	0.963	0.375	0.256	0.042	0.045	0.052	0.010	0.007
NO	0.632	0.656	0.971	0.339	0.315	0.041	0.044	0.051	0.010	0.007
Substituent	KSCI <sub>GS1</sub>	KSCI <sub>GS2</sub>	KSCI <sub>TS</sub>	$\Delta$ KSCI <sub>1</sub>	$\Delta$ KSCI <sub>2</sub>	SCI <sub>GS1</sub>	SCI <sub>GS2</sub>	SCI <sub>TS</sub>	$\Delta$ SCI <sub>1</sub>	$\Delta$ SCI <sub>2</sub>
OH	5.19	2.94	5.32	0.13	2.38	15.18	9.07	15.59	0.41	6.52
F	5.26	3.09	6.20	0.94	3.11	14.85	9.68	17.86	3.01	8.18
NH <sub>2</sub>	4.23	2.91	5.44	1.21	2.53	12.68	9.060	16.57	3.89	7.510
CH <sub>3</sub>	3.97	3.61	6.69	2.72	3.08	12.87	11.72	22.11	9.24	10.39
CN	3.45	3.57	6.58	3.13	3.01	11.00	12.04	21.75	10.75	9.710
NO <sub>2</sub>	4.24	3.52	7.12	2.88	3.60	12.27	11.67	21.86	9.59	10.19
CHO	3.41	3.58	6.78	3.37	3.20	10.95	12.08	22.60	11.65	10.52
NO	3.67	3.59	7.02	3.35	3.43	11.17	11.94	22.49	11.32	10.55

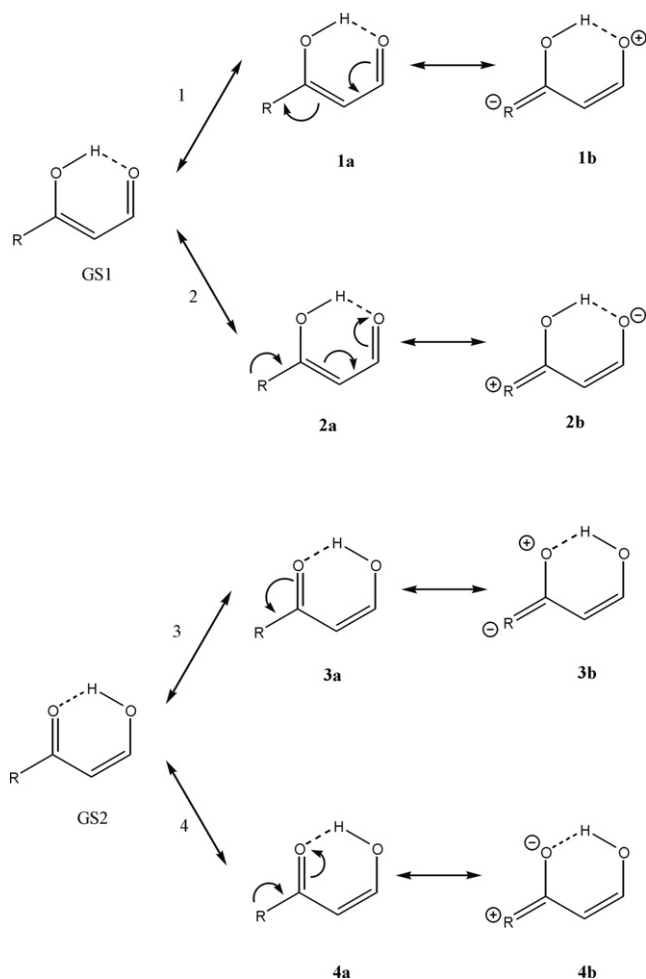
PDI in a.u., SCI and KSCI in 10<sup>-4</sup> a.u.

Fig. 4. Schematic representation of resonance (mesomeric) effect in malonaldehyde systems substituted at position 1(3).

is not the carbon, then GS1 system is significantly less stable since field/inductive substituents with positive  $F$  values disfavours GS1 as compared to the GS2 one.

In the previous part of the discussion, devoted to malonaldehyde substituted at position 2, there were relations between  $\Delta E^\ddagger$  (measured as the energy difference between TS and GS) and the parameters of the H-bridge. In this case there is a similar situation. This time, however, two sets of  $\Delta E^\ddagger$  have to be considered:  $\Delta E_1^\ddagger = E_{TS} - E_{GS1}$  and  $\Delta E_2^\ddagger = E_{TS} - E_{GS2}$  (see Table 4). Interestingly,  $\Delta E_1^\ddagger$  correlates only with H-bridge parameters corresponding to the GS1 geometry, while  $\Delta E_2^\ddagger$  correlates with suitable parameters of the H-bridge in GS2. This includes also delocalization indices estimated for bonds forming H-bridges in GS1 and GS2, respectively. In Fig. 5 the relations between  $\Delta E^\ddagger$  and selected geometrical parameters of H-bridge have been illustrated on suitable diagrams. Likewise for previous systems (substituted at position 2), there is a lack of direct relation between  $\Delta E^\ddagger$  values and absolute values of aromaticity indices. However, as distinct from previous case, in this case there are also very poor correlations if considering changes of aromaticity from GS to TS, especially in the case of GS2 (see Fig. 6 for some graphical representation). This is in agreement with the aforementioned fact that substituents attached to GS2 affect H-bridge mainly through the field/inductive effect and the influence of H-bridge through resonance is strongly limited. Some poor relation can be found only for GS1, in the case of which the resonance effect seems to be more effective. As aromaticity indices indicate, TSs are more delocalized than GSs. However, there are also large differences in the *quasi*-aromatic character, if considering both GSs. For systems substituted with carbon substituents both GSs are characterized by relatively close values of aromaticity indices. For these systems, in which the C–R bond can be considered as polarised bond, the GS1 system is significantly more delocalized than GS2. This is connected with shorter distances in H-bridge, as discussed above. Finally, GS2 systems with electron donating substituents are the less aromatic because of the relevance of structure 4b.

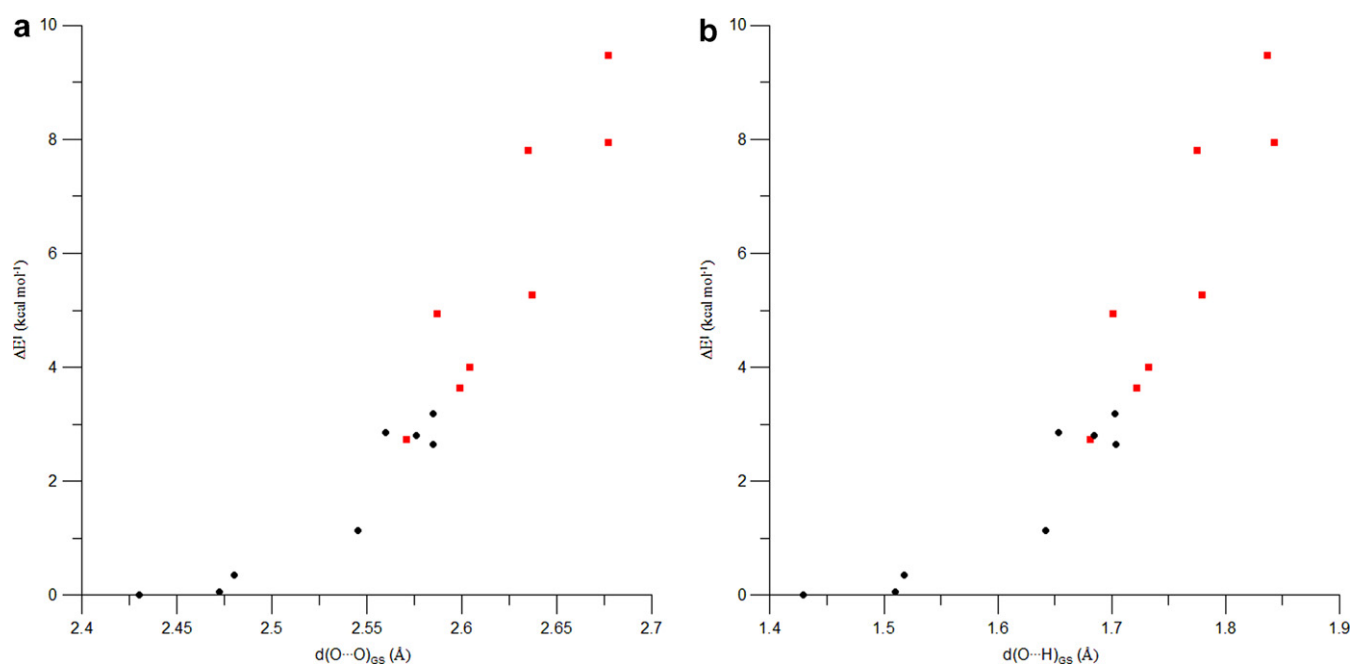


Fig. 5. Interdependences between  $\Delta E^{\ddagger}$  and geometrical parameters of H-bridge. Circles correspond to  $\Delta E_1^{\ddagger} = E_{TS} - E_{GS1}$  vs. geometrical parameter of GS1, squares to  $\Delta E_2^{\ddagger} = E_{TS} - E_{GS2}$  vs. geometrical parameter of GS2.

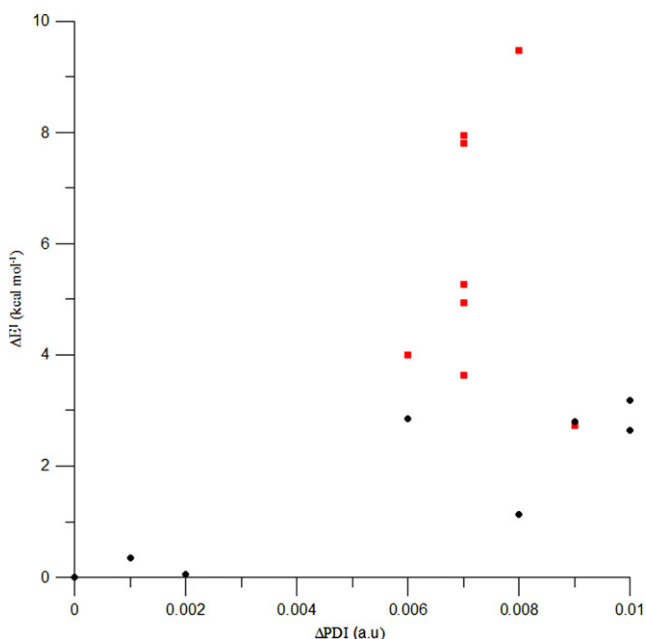


Fig. 6. Interdependences between  $\Delta E^{\ddagger}$  and  $\Delta PDI$ . Circles correspond to  $\Delta E_1^{\ddagger}(E_{TS} - E_{GS1})$  vs.  $PDI_{(TS-GS1)}$ , squares to  $\Delta E_2^{\ddagger}(E_{TS} - E_{GS2})$  vs.  $PDI_{(TS-GS2)}$ .

The correlation coefficients estimated for linear regressions reflecting mutual interrelations between substituent constants and selected parameters of systems under discussion can be found in Table S2 of the Supporting information. It is found that in the case of GS1 the main influence of substituent on H-bridge proceeds through the resonance effect, what can be confirmed by relatively large values for relations estimated for  $R$  constants. However, in the case of

GS2, the main effect seems to be a field/inductive one. The largest values of suitable correlation coefficients have been found for the constant  $F$ . This concerns the H-bridge parameters, however in the case of *quasi*-aromaticity in both GS1 and GS2 the resonance effect predominates over a field/inductive one.

#### 4. Conclusions

It has been shown, that substituents attached to the malonaldehyde moiety influence both the intramolecular HB as well as the *quasi*-aromatic character of the *quasi*-ring formed due to HB formation. The substituent effect depends not only from the kind of substituent, but also from its position in the molecule. When the substituent is attached at the position 2 of *quasi*-ring, the resonance effect predominates over the field/inductive effect which leads to changes in H-bonding and *quasi*-aromaticity of the ring motif. In the case of 1(3) substitution the field/inductive effect is significantly more effective influencing the HB strength. Interestingly, the field/inductive effect stabilizes the GS2 structure while, at the same time, disfavoring the H-bonding and reducing the aromaticity of the *quasi*-ring. In this case, like in the previous one, the *quasi*-aromaticity mainly depends on the resonance effect. For the GS2 isomer, the aromaticity of the *quasi*-ring is especially low for electron-donating substituents. Finally, it can be also stated, that the transition forms of the systems under consideration are more aromatic/delocalized if comparing with ground state forms. Thus, the delocalization of electrons within the *quasi*-ring of malonaldehyde clearly favours the proton transfer reaction.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemphys.2007.09.016](https://doi.org/10.1016/j.chemphys.2007.09.016).

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