

## Semiempirical Study of Intramolecular Hydrogen Bond in 6-Hydroxy-2-formylfulvene and 9-Hydroxyphenalenone

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It is shown that semiempirical MINDO/3, MNDO and AM1 methods are very useful in discussing intramolecular hydrogen bonding in sizeable systems. The present results indicate that intramolecular H-bonds in 6-hydroxy-2-formylfulvene and 9-hydroxyphenalenone are asymmetric, in full accordance with ESCA observations and DQCC measurements. The former molecule should exhibit a stronger H-bond. On the other hand, the barrier height for proton tunnelling is higher in the latter compound. Relative stabilities of various species are interpreted by employing the energy partitioning technique.

### INTRODUCTION

A family of  $\beta$ -diketones exhibits pronounced chelating properties and forms coordination complexes with almost every metal in the periodic table. Their enol forms possess intramolecular hydrogen bond(s) which have interesting static and dynamic features. Concomitantly, these systems continue to attract considerable attention. In the preceding paper, which dealt with naphthazarin, a comprehensive survey of the literature was given.<sup>1</sup> Therefore, it will not be repeated here. We now present the results of the semiempirical study of 6-hydroxy-2-formylfulvene (6-HFF) and 9-hydroxyphenalenone (9-HPO). Unlike naphthazarin, they possess a single intramolecular hydrogen bond which is a part of seven- and six- atom moieties, respectively. Both systems seem to have very short bridgehead  $O \cdots O$  distances of the H-bond.<sup>2,3</sup> As a part of our larger project of investigating intramolecular hydrogen bonds, we performed MINDO/3<sup>4</sup>, MNDO<sup>5</sup> and AM1<sup>6</sup> calculations on these compounds. Contrary to a widespread opinion that MINDO/3 and MNDO methods fail to provide a satisfactory description of hydrogen bonding,<sup>7-9</sup> we were pleasantly surprised by their performance in studying  $\beta$ -diketones. Whereas the former is true for intermolecular H-bonds, we found that MINDO/3 and MNDO methods reproduce very well  $O \cdots H-O$  internal hydrogen bonds. For example, they give a correct ordering of the stability of vitamin C tautomers and offer a good qualitative interpretation of their main features.<sup>10</sup> The same holds for a number of 3-substituted tetronic and 3-acetyl tetramic acids.<sup>11</sup> A recent study has conclusively shown

that this type of semiempirical approach reproduces quite well gross properties of archetypic systems malonaldehyde (MA) and acetylacetone (ACAC) and complex molecules like naphthazarin tautomers.<sup>1</sup> The results were in good accordance with reliable experimental data. Hence, extension of this work to other intramolecularly H-bonded systems, such as 6-hydroxy-2-formyl fulvene and 9-hydroxyphenalenone, is fully justified.

## RESULTS AND DISCUSSION

The studied molecules are schematically shown in Figures 1 and 2. Before our results are discussed, a brief account of the present state of affair will be given. Solid state X-ray and neutron diffraction data indicate that 6-hydroxy-2-formylfulvene (*1*) has a slightly asymmetric H-bond with two O—H distances of 1.214 Å and 1.343 Å.<sup>2</sup> On the other hand, <sup>1</sup>H NMR data<sup>12</sup> are compatible with *C*<sub>2v</sub> symmetry of *1*, but the IR spectrum can be interpreted by rapidly interconverting *C*<sub>s</sub> forms,<sup>12</sup> too. Gas-phase microwave spectra do not give an unequivocal answer.<sup>13</sup> Both possibilities, *C*<sub>2v</sub> form and fast proton oscillations ( $\sim 2 \cdot 10^{12}$  s<sup>-1</sup>) between two equivalent *C*<sub>s</sub> structures may arise. The most conclusive piece of evidence that *1* has *C*<sub>s</sub> symmetry was provided by the X-ray PES (ESCA) study.<sup>14</sup> As it is well known, an ESCA snapshot is very fast ( $10^{-16}$  s) yielding an instantaneous picture of a molecule.

The crystalline X-ray measurement of 9-HPO showed a very short O · · · O bridgehead distance of 2.486 Å indicating a strong hydrogen bond.<sup>3</sup> However, the data do not allow accurate determination of the position of the hydrogen-bonded proton. Gas-phase ESCA spectra unambiguously show two nonequivalent O atoms being consistent with *C*<sub>s</sub> symmetry.<sup>14</sup> Additional support is provided by deuteron electric field gradient and related quadrupole coupling constant (DQCC) study<sup>15</sup> which is consistent with a rapid exchange between two asymmetric potential wells. In contrast, <sup>1</sup>H and <sup>13</sup>C NMR studies of 9-HPO indicate *C*<sub>2v</sub> symmetry in solution down to 130 K, but rapidly interconverting *C*<sub>s</sub> forms cannot be ruled out.<sup>14</sup> Further, the solution and solid state IR study found no characteristic O—H stretching frequency.<sup>16</sup>

It follows that the structures of 6-HFF and 9-HPO might well depend on the phase. We are inclined to believe that the asymmetric H-bond is definitely the most stable form, at least in vapour. This conclusion is based on the semiempirical results discussed below.

The calculated  $\Delta H_f$  values for systems 1—6 are presented in Table I. The most stable conformation of 6-hydroxy-2-formylfulvene is *1* in accordance with the general idea of the structure of this molecule. It is interesting that all three methods indicate that the symmetric single well H-bond is considerably less stable. The difference in energy  $E(2)$ — $E(1)$  is 17.6, 26.6 and 15.5 (in kcal mol<sup>-1</sup>) as estimated by MINDO/3, MNDO and AM1 methods, respectively. This barrier height will be lowered by electron correlation, but a very dramatic effect is not expected in view of the *ab initio* results on MA<sup>17\*</sup>. Hence, semiempirical results lend a support to experimental findings

\* See however Ref. (22) where full CI with a basis set slightly better than DZ gives the barrier of 8.0 kcal mol<sup>-1</sup>.

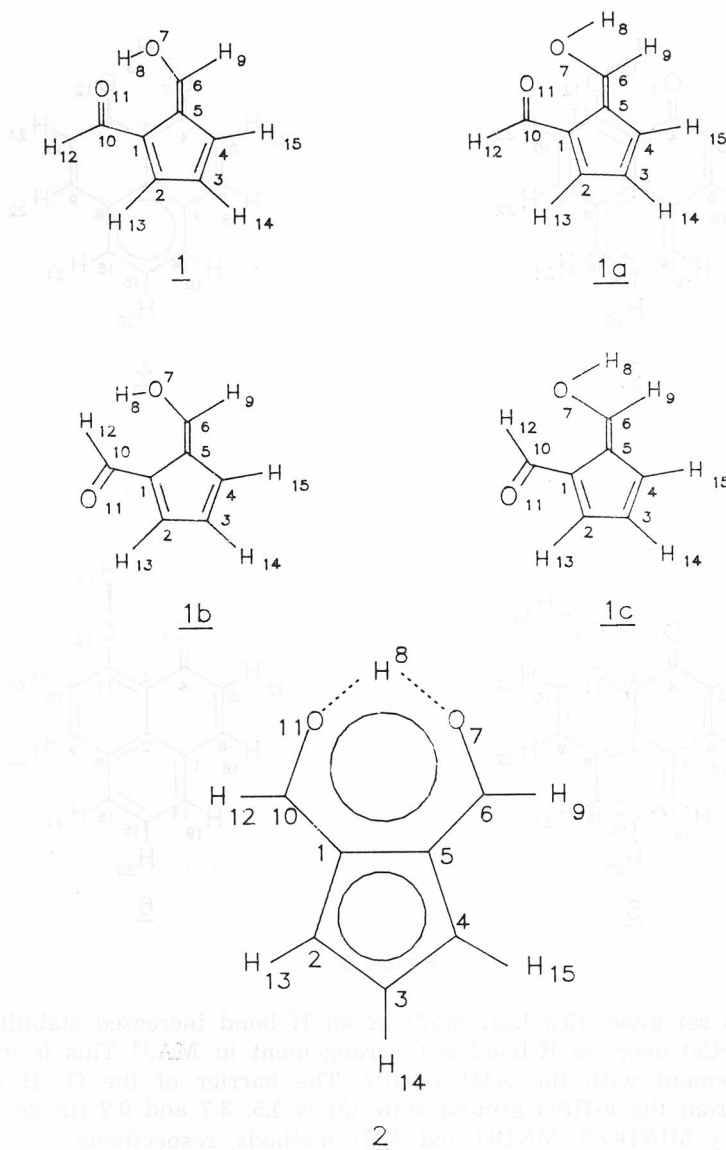


Figure 1.

which suggest an asymmetric H-bond. Further, the AM1 difference  $E(1a) - E(1) \sim 10 \text{ kcal mol}^{-1}$  gives some information about the strength of the intramolecular hydrogen bond. It seems that the H-bond strength in 9-HPO is smaller, as evidenced by the AM1 estimate ( $\sim 7 \text{ kcal mol}^{-1}$ ). This point will be discussed in more detail later on. MINDO/3 and MNDO methods correctly predict that form 3 is more stable than 5, but the calculated energy difference is small ( $\sim 2 \text{ kcal mol}^{-1}$ ) and very likely it is too small. Let us mention that

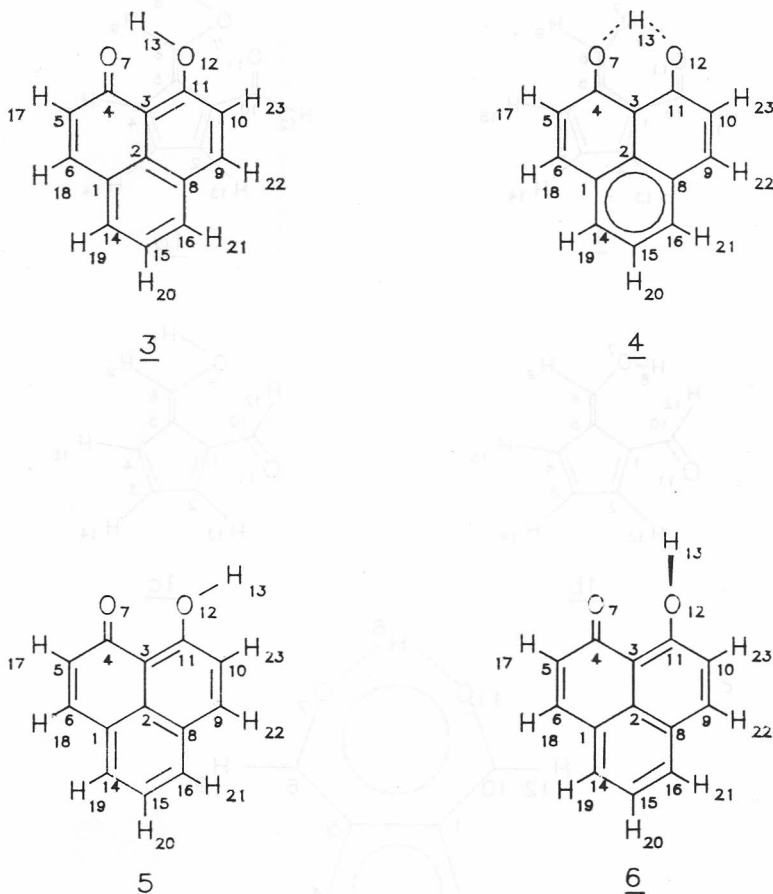


Figure 2.

4-31G basis set gives  $13.3 \text{ kcal mol}^{-1}$  as an H bond increased stability (conformation cCc) over no H-bond cCt arrangement in MA.<sup>18</sup> This is in qualitative agreement with the AM1 results. The barrier of the O—H rotation measured from the 9-HPO ground state (3) is 5.5, 3.7 and 9.2 (in  $\text{kcal mol}^{-1}$ ) estimated by MINDO/3, MNDO and AM1 methods, respectively.

Structural parameters and bicentric energy terms for compounds 1—2 are given in Table II. Only MNDO and AM1 values are given because they are supposed to be somewhat more realistic. Two-center energy terms will give an insight into the strength of chemical bonds and interatomic interactions in general.<sup>19-21</sup> Comparison of MA and ACAC geometries estimated by MNDO and AM1 methods with *ab initio* data<sup>1</sup> has shown that semiempirical treatments offer a reasonable description of the shape and size of  $\beta$ -diketones. Their information, however, is more qualitative than quantitative. Nevertheless, gross features are well reproduced, which is sufficient

TABLE I

Heats of formation of 6-hydroxy-2-formylfulvene and 9-hydroxyphenalenone, as calculated by MINDO/3, MNDO and AM1 methods (kcal mol<sup>-1</sup>)

Molecule	MINDO/3	MNDO	AM1
1	-26.5	-30.1	-23.8
1a	-26.0	-27.3	-13.4
1b	-26.2	-28.1	-18.6
1c	-26.3	-28.9	-16.8
2	- 8.9	- 3.5	- 8.3
3	-21.3	-26.6	-20.3
4	- 1.4	5.1	6.6
5	-19.1	-24.7	-13.1
6	-15.8	-22.9	-11.1

for our purpose. The hydrogen bonded enol form 1 has a slightly more pronounced delocalization as compared to prototype MA.<sup>1</sup> The generally accepted assumption that the internally H-bonded form possesses enhanced delocalization seems to be justified as evidenced by comparison of structures 1 and 1a. Agreement of the parent molecule 1 with neutron diffraction data of Fuess and Lindner<sup>2</sup> is poor. Accordance with their X-ray findings is even worse. Experimental values do exhibit asymmetric bonds (C<sub>s</sub>) but their differences are small. Both MNDO and AM1 methods yield clearly localized structure of 1 and we believe they are essentially correct. More accurate *ab initio* calculations are desirable and we are planning them. Preliminary STO-3G results for the symmetrical form 2 are in pretty good agreement with semiempirical values presented in Table II. The symmetric C<sub>2v</sub> geometry 2 has intermediate bond distances between single and double bonds exhibiting very strong delocalization. »Chemical intuition« based on oversim-

TABLE II

Structural parameters and bicentric energy terms in 6-hydroxy-2-formylfulvene systems 1-2, as estimated by MNDO and AM1 methods (in Å, degrees and eV, respectively)

Molecule	Atomic pairs	MNDO		AM1		EXPTL.
		Distance or angle	E <sub>AB</sub>	Distance or angle	E <sub>AB</sub>	Distance or angle
1	C <sub>2</sub> =C <sub>1</sub>	1.389	-21.9	1.387	-20.9	1.411 <sup>a</sup>
	C <sub>1</sub> -C <sub>5</sub>	1.486	-16.5	1.469	-15.7	1.462
	C <sub>5</sub> =C <sub>6</sub>	1.373	-22.4	1.356	-21.6	1.386
	C <sub>2</sub> -C <sub>3</sub>	1.456	-17.2	1.454	-16.7	1.408
	C <sub>3</sub> =C <sub>4</sub>	1.371	-22.4	1.373	-21.6	1.403
	C <sub>4</sub> -C <sub>5</sub>	1.484	-16.4	1.471	-15.9	1.408
	C <sub>1</sub> -C <sub>10</sub>	1.475	-16.7	1.447	-16.2	1.391
	C <sub>6</sub> -C <sub>7</sub>	1.333	-18.8	1.343	-17.4	1.274
	C <sub>10</sub> =C <sub>11</sub>	1.225	-27.0	1.239	-25.1	1.253
	O <sub>7</sub> -H <sub>8</sub>	0.946	-14.0	0.975	-12.5	

Table II (contd.)

Molecule	Atomic pairs	MNDO	AM1		EXPTL.
		Distance or angle	$E_{AB}$	Distance or angle	$E_{AB}$
	C <sub>10</sub> —H <sub>12</sub>	1.113	—12.4	1.117	—12.0
	O <sub>11</sub> ...H <sub>8</sub>	2.260	—0.4	1.935	—1.0
	O <sub>7</sub> ...O <sub>11</sub>	3.091	0.3	2.861	0.3
	C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	110.0°	—	109.3°	—
	C <sub>2</sub> —C <sub>1</sub> —C <sub>5</sub>	107.4°	—	107.9°	—
	C <sub>1</sub> —C <sub>5</sub> —C <sub>4</sub>	105.0°	—	105.4°	—
	C <sub>1</sub> —C <sub>5</sub> —C <sub>6</sub>	135.5°	—	133.6°	—
	C <sub>5</sub> —C <sub>1</sub> —C <sub>10</sub>	130.9°	—	129.8°	—
	C <sub>1</sub> —C <sub>10</sub> —C <sub>11</sub>	126.6°	—	125.9°	—
	C <sub>5</sub> —C <sub>6</sub> —C <sub>7</sub>	131.4°	—	129.5°	—
	C <sub>6</sub> —C <sub>7</sub> —C <sub>8</sub>	117.3°	—	111.7°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	108.0°	—	108.2°	—
	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	109.6°	—	109.2°	—
<i>1a</i>	C <sub>1</sub> —C <sub>2</sub>	1.384	—22.1	1.379	—21.3
	C <sub>1</sub> —C <sub>5</sub>	1.487	—16.3	1.471	—15.7
	C <sub>5</sub> —C <sub>6</sub>	1.368	—22.7	1.352	—21.9
	C <sub>2</sub> —C <sub>3</sub>	1.461	—16.9	1.463	—16.3
	C <sub>3</sub> —C <sub>4</sub>	1.369	—22.5	1.369	—21.8
	C <sub>4</sub> —C <sub>5</sub>	1.485	—16.4	1.473	—15.8
	C <sub>1</sub> —C <sub>10</sub>	1.479	—16.4	1.454	—15.8
		MNDO	AM1		
		Distance or angle	$E_{AB}$	Distance or angle	$E_{AB}$
<i>1a</i>	C <sub>6</sub> —O <sub>7</sub>	1.343	—18.3	1.359	—16.7
	C <sub>10</sub> —O <sub>11</sub>	1.222	—27.3	1.233	—25.6
	O <sub>7</sub> —H <sub>8</sub>	0.949	—14.0	0.969	—12.3
	O <sub>11</sub> ...H <sub>8</sub>	3.633	—0.3	3.294	—0.3
	O <sub>7</sub> ...O <sub>11</sub>	2.819	0.5	2.464	0.4
	C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	110.4°	—	109.0°	—
	C <sub>2</sub> —C <sub>1</sub> —C <sub>5</sub>	—	—	108.1°	—
	C <sub>1</sub> —C <sub>5</sub> —C <sub>4</sub>	—	—	105.6°	—
	C <sub>1</sub> —C <sub>5</sub> —C <sub>6</sub>	—	—	131.6°	—
	C <sub>5</sub> —C <sub>1</sub> —C <sub>10</sub>	—	—	127.5°	—
	C <sub>1</sub> —C <sub>10</sub> —C <sub>11</sub>	127.3°	—	125.7°	—
	C <sub>5</sub> —C <sub>6</sub> —C <sub>7</sub>	123.6°	—	120.8°	—
	C <sub>6</sub> —C <sub>7</sub> —C <sub>8</sub>	123.6°	—	107.9°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	107.7°	—	108.4°	—
	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	109°	—	108.9°	—
<i>2</i>	C <sub>1</sub> —C <sub>2</sub>	1.426	—19.3	1.463	—18.5
	C <sub>1</sub> —C <sub>5</sub>	1.474	—16.5	1.400	—15.9
	C <sub>5</sub> —C <sub>6</sub>	1.424	—22.4	1.565	—18.9
	C <sub>2</sub> —C <sub>3</sub>	1.413	—19.8	1.410	—19.2
	C <sub>3</sub> —C <sub>4</sub>	1.413	—19.8	1.410	—19.2
	C <sub>4</sub> —C <sub>5</sub>	1.426	—19.3	1.436	—18.5
	C <sub>1</sub> —C <sub>10</sub>	1.424	—19.5	1.400	—18.9

Table II (contd.)

Molecule	Atomic pairs	MNDO	$E_{AB}$	AM1	$E_{AB}$
		Distance or angle		Distance or angle	
2	C <sub>6</sub> —O <sub>7</sub>	1.274	—23.4	1.300	—21.6
	C <sub>10</sub> —O <sub>11</sub>	1.274	—23.4	1.300	—21.6
	O <sub>7</sub> ...H <sub>8</sub>	1.195	—7.0	1.328	—6.6
	O <sub>11</sub> ...H <sub>8</sub>	1.195	—7.0	1.328	—6.6
	O <sub>7</sub> ...O <sub>11</sub>	3.181	0.9	2.349	0.6
	C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	109.2°	—	108.8°	—
	C <sub>2</sub> —C <sub>1</sub> —C <sub>5</sub>	106.6°	—	109.4°	—
	C <sub>1</sub> —C <sub>5</sub> —C <sub>4</sub>	106.6°	—	109.4°	—
	C <sub>1</sub> —C <sub>5</sub> —C <sub>6</sub>	126.8°	—	125.3°	—
	C <sub>5</sub> —C <sub>1</sub> —C <sub>10</sub>	126.8°	—	125.3°	—
	C <sub>1</sub> —C <sub>10</sub> —O <sub>11</sub>	124.°	—	125.2°	—
	C <sub>5</sub> —C <sub>6</sub> —O <sub>7</sub>	124.4°	—	125.2°	—
	C <sub>6</sub> —O <sub>7</sub> —H <sub>8</sub>	108.3°	—	114.2°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	108.6°	—	108.5°	—
	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	109.2°	—	108.8°	—

<sup>a</sup> Neutron diffraction data<sup>2</sup>.

plified MO schemes says that delocalized structures are very stable. In fact, the C<sub>s</sub> geometry with pronounced localization represents the ground state of the molecule as mentioned above.

Energy partitioning is a useful tool in interpreting relative stabilities. Let's consider the AM1 results and denote the total directly bonded two-center term, nonbonding two-electron interactions, and single-center energy as  $E_2^t$  (b),  $E_2^t$  (nb) and  $E_1^t$ , respectively. We can call this apportioning of the total energy as gross energy partitioning. Then, the corresponding AM1 values for *1* and *1a* read (in eV): —245.888 (—245.725), 6.124 (6.697) and —1378.150 (—1378.436), respectively, where the *1a* energy components are given within parentheses. One observes that the single-center term dominates, followed by two-center bonding interactions, whereas nonbonding interactions are smaller by 3 or 2 orders of magnitude. Nevertheless, generally they cannot be neglected in quantitative considerations as we shall see shortly. The differences in various energy terms between *1a* and *1* are (in eV):

$$E(1a) - E(1): \quad \frac{E_2^t(b)}{0.16} \quad \frac{E_2^t(nb)}{0.57} \quad \frac{E_1^t}{-0.29}$$

It appears that the difference in the nonbonding term  $E_2^t$ (nb) is the largest (0.57 eV). Examination of the data shows that the interaction of hydrogen atom H<sub>8</sub> with oxygen O<sub>11</sub> is —0.98 eV and —0.28 eV in *1* and *1a*. Note that

these two atoms are formally treated as nonbonded in both forms for the sake of consistency. The difference of 0.7 eV gives the largest share of the instability of *1a* relative to *1*. A more precise value of 0.44 eV ( $\sim 10.1$  kcal mol<sup>-1</sup>) is obtained if it is taken into account that the *1a* form has lower one-center total energy ( $-0.29$  eV) whilst two-center bonding is slightly more pronounced in the ground state *1*.

It would be of interest to understand the difference in stability between the ground state *1* and the much debated symmetric H-bond form *2*. For this purpose it is convenient to include the »nonbonding« pair interaction  $H_8 \cdots O_{11}$  into bonding pairs. The total energy components for *1* and *2* read:  $E_2^t(b) = -246.87$  ( $-247.40$ ),  $E_2^t(nb) = 7.10$  ( $7.31$ ) and  $E_1^t = -1378.15$  ( $-1377.15$ ), where the corresponding values for the symmetric form *2* are given within parentheses. One observes that the two-center energy of directly bonded atoms is lower in the delocalized symmetric form *2*, but it has a slightly increased amount of nonbonding interactions and, more importantly, a substantially higher sum of one-center energies. The question arises whether these changes are spread out over the whole molecular skeleton or one can indentify dominant differences in a particular molecular fragment like *e.g.* the hydrogen bridge and its immediate neighbourhood. Careful examination of data shows that localized bonds in *1*, which become equivalent in delocalized form *2*, do not significantly change their average energy, with one exception. For example,  $E_{12}$  and  $E_{45}$  bond energies in *1* assume the values of  $-20.92$  eV and  $-16.00$  eV, respectively. Their average  $-18.46$  eV matches exactly the energy of two equivalent  $C_1-C_2$  and  $C_4-C_5$  bonds in *2*. However, it appears that two delocalized C—O bonds in *2* are more stable by  $\sim 0.6$  eV than their localized  $C_6-O_7$  and  $C_{10}=O_{11}$  counterparts in the ground state *1*. This is the main reason why *2* has lower total two-center energy. Other relatively small changes in energy nearly cancel out. Analysis of one-center energy terms shows that atoms  $C_6$  and  $C_{10}$  are more stable in the ground state *1* by  $\sim 0.6$  eV on average. Additional substantial contribution to the stability of the asymmetric form comes from the hydrogen bonded proton. In the  $O \cdots H-O$  situation single-center energy of hydrogen (in *1*) is by  $\sim 0.5$  lower than in the symmetric delocalized arrangement  $O \cdots H \cdots O$ . Again, slight variations in one-center atomic terms for other molecular sites tend to cancel.

It is very difficult, if not impossible, to recognize dominant interactions in the nonbonded term. In the first place, the latter involves positive and negative contributions implying that there are long range stabilizing effects too. Their general characteristics is that they are all relatively small, but their variation is pronounced, presumably due to the differences in formal atomic charges and concomitant changes in Coulomb interactions. For instance, there is a significant increase in repulsion between hydrogen  $H_8$  with carbons  $C_6$  and  $C_{10}$  in the symmetric form *2*. Concomitantly there is a decrease in energy of interaction between  $H_8$  and carbons  $C_1$  and  $C_5$  relative to *1*. This can be explained by a redistribution of charge in the symmetric H-bond *2* (*vide infra*). Namely, the  $H_8$  atom becomes more positive in *2* as well as  $C_6$  and  $C_{10}$  sites. Contrary to that,  $C_1$  and  $C_5$  positions carry more electron density. We conclude that the  $E_2^t(nb)$  term is the result of an interplay between a large number of relatively small numbers. Further, the difference in  $E_2^t(nb)$  between



1 and 2 is not highly pronounced and can be neglected in a qualitative discussion. Hence, it follows that the localized form 1 is more stable than the symmetric delocalized arrangement 2, because the increase in one-center energy of H<sub>8</sub>, C<sub>6</sub> and C<sub>10</sub> atoms in 1 outweighs the decrease in delocalization energy of bonds C<sub>6</sub>—C<sub>7</sub> and C<sub>10</sub>—C<sub>11</sub> in 2.

9-hydroxyphenalenone (Table III) seems to have a shorter O...O distance than 6-hydroxy-2-formylfulvene according to MNDO and AM1 calculations. Although both methods give notoriously too long bridgehead O...O distances of internally hydrogen-bonded bridges by 0.60—0.62 Å (MNDO) and 0.27—0.29 Å (AM1) as estimated by results in MA where an isotopic range of 2.553—2.576 Å was reported<sup>23</sup>. They give useful information about O...O contacts. If we adopt these empirical corrections then the O...O distance in 1 would be roughly 2.47—2.49 Å and 2.57—2.59 Å by MNDO and AM1 methods, respectively. The corresponding values in 3 would read 2.27—2.29 Å and 2.46—2.48 Å. The latter AM1 estimate is quite close to the X-ray value of 2.486 Å<sup>3</sup>.

TABLE III

Selected structural parameters and bicentric energy terms in 9-hydroxyphenalenone system 3—6, as estimated by MNDO and AM1 methods (in Å, degrees and eV, respectively)

Molecule	Atomic pairs	MNDO		AM1		EXPTL.
		Distance or angle	$E_{AB}$	Distance or angle	$E_{AB}$	Distance or angle
3	C <sub>3</sub> —C <sub>4</sub>	1.501	—16.5	1.468	—16.2	1.427 <sup>a</sup>
	C <sub>3</sub> —C <sub>11</sub>	1.414	—20.9	1.396	—20.1	1.415
	C <sub>4</sub> =O <sub>7</sub>	1.233	—26.5	1.428	—24.7	1.290
	C <sub>11</sub> —O <sub>12</sub>	1.346	—18.5	1.359	—17.0	1.297
	O <sub>12</sub> ...H <sub>13</sub>	0.946	—14.1	0.974	—12.6	1.26
	O <sub>7</sub> ...H <sub>13</sub>	2.213	—0.4	1.960	—1.0	1.31
	C <sub>4</sub> —C <sub>5</sub>	1.489	—16.2	1.468	—15.9	1.417
	C <sub>10</sub> —C <sub>11</sub>	1.456	—18.0	1.433	—17.6	1.415
	C <sub>2</sub> —C <sub>3</sub>	1.458	—18.2	1.431	—17.8	1.417
	C <sub>5</sub> =C <sub>6</sub>	1.350	—23.4	1.344	—22.7	1.342
	C <sub>9</sub> =C <sub>10</sub>	1.370	—22.1	1.364	—21.4	1.342
	C <sub>1</sub> —C <sub>2</sub>	1.449	—18.3	1.427	—17.9	1.413
	C <sub>2</sub> —C <sub>8</sub>	1.434	—19.4	1.418	—18.7	1.415
	C <sub>1</sub> —C <sub>6</sub>	1.465	—16.8	1.448	—16.2	1.432
	C <sub>8</sub> —C <sub>9</sub>	1.443	—18.0	1.425	—17.5	1.422
	C <sub>1</sub> —C <sub>14</sub>	1.400	—20.8	1.387	—20.1	1.391
	C <sub>8</sub> —C <sub>16</sub>	1.428	—18.7	1.414	—18.2	1.393
	C <sub>14</sub> —C <sub>15</sub>	1.416	—19.0	1.408	—18.6	1.374
	C <sub>15</sub> =C <sub>16</sub>	1.386	—21.2	1.379	—20.4	1.360
	O <sub>7</sub> ...O <sub>12</sub>	2.885	0.3	2.751	0.3	2.486
	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	117.8°	—	117.6°	—	118.4°
	C <sub>4</sub> —C <sub>3</sub> —C <sub>11</sub>	124.0°	—	122.4°	—	119.7°
	C <sub>3</sub> —C <sub>11</sub> —C <sub>10</sub>	120.8°	—	120.9°	—	118.6°
	C <sub>3</sub> —C <sub>4</sub> —O <sub>7</sub>	122.5°	—	122.2°	—	120.6°
	C <sub>3</sub> —C <sub>11</sub> —O <sub>12</sub>	127.2°	—	125.8°	—	120.9°
	C <sub>11</sub> —O <sub>12</sub> —H <sub>13</sub>	117.3°	—	110.9°	—	97°
	C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	122.2°	—	121.9°	—	121.5°
	C <sub>9</sub> —C <sub>10</sub> —C <sub>11</sub>	120.4°	—	120.0°	—	121.2°
	C <sub>1</sub> —C <sub>2</sub> —C <sub>8</sub>	118.0°	—	118.6°	—	120.3°
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	117.9°	—	119.0°	—	120.0°
	C <sub>2</sub> —C <sub>3</sub> —C <sub>11</sub>	118.1°	—	118.6°	—	120.4°

Table III (contd.)

Molecule	Atomic pairs	MNDO	$E_{AB}$	AM1	$E_{AB}$
		Distance or angle		Distance or angle	
4	C <sub>3</sub> —C <sub>4</sub>	1.448	—19.0	1.426	—18.4
	C <sub>3</sub> —C <sub>11</sub>	1.448	—19.0	1.426	—18.4
	C <sub>4</sub> =O <sub>7</sub>	1.287	—22.7	1.300	—21.0
	C <sub>11</sub> —O <sub>12</sub>	1.287	—22.7	1.300	—21.0
	O <sub>12</sub> ...H <sub>13</sub>	1.222	— 6.9	1.241	—6.6
	O <sub>7</sub> ...H <sub>13</sub>	1.222	— 6.9	1.241	— 6.6
	C <sub>4</sub> —C <sub>5</sub>	1.464	—17.3	1.449	—16.8
	C <sub>10</sub> —C <sub>11</sub>	1.464	—17.3	1.449	—16.8
	C <sub>2</sub> —C <sub>3</sub>	1.435	—18.7	1.416	—18.1
	C <sub>5</sub> =C <sub>6</sub>	1.368	—22.7	1.361	—22.2
	C <sub>9</sub> =C <sub>10</sub>	1.368	—22.7	1.361	—22.2
	C <sub>1</sub> —C <sub>2</sub>	1.437	—18.9	1.419	—18.3
	C <sub>2</sub> —C <sub>8</sub>	1.437	—18.9	1.419	—18.3
	C <sub>1</sub> —C <sub>6</sub>	1.459	—17.4	1.451	—16.5
	C <sub>8</sub> —C <sub>9</sub>	1.459	—17.4	1.451	—16.5
	C <sub>1</sub> —C <sub>14</sub>	1.414	—19.8	1.400	—19.2
	C <sub>8</sub> —C <sub>16</sub>	1.414	—19.8	1.400	—19.2
	C <sub>14</sub> —C <sub>15</sub>	1.404	—20.1	1.394	—19.5
	C <sub>15</sub> —C <sub>16</sub>	1.404	—20.1	1.394	—19.5
	O <sub>7</sub> ...O <sub>12</sub>	2.345	0.8	2.378	0.6
	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	118.3°	—	118.8°	—
	C <sub>4</sub> —C <sub>3</sub> —C <sub>11</sub>	117.8°	—	118.0°	—
	C <sub>3</sub> —C <sub>11</sub> —C <sub>10</sub>	118.3°	—	118.8°	—
	C <sub>3</sub> —C <sub>4</sub> —O <sub>7</sub>	118.1°	—	119.5°	—
	C <sub>3</sub> —C <sub>11</sub> —O <sub>12</sub>	118.1°	—	119.5°	—
	C <sub>11</sub> —O <sub>12</sub> —H <sub>13</sub>	109.4°	—	108.1°	—
	C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	119.9°	—	119.6°	—
	C <sub>9</sub> —C <sub>10</sub> —C <sub>11</sub>	119.9°	—	119.6°	—
	C <sub>1</sub> —C <sub>2</sub> —C <sub>8</sub>	121.0°	—	121.0°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	121.1°	—	121.1°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>11</sub>	121.1°	—	120.8°	—
	5	C <sub>3</sub> —C <sub>4</sub>	1.504	—16.2	1.475
C <sub>3</sub> —C <sub>11</sub>		1.415	—20.8	1.395	—20.0
C <sub>4</sub> =O <sub>7</sub>		1.230	—26.8	1.239	—16.5
C <sub>11</sub> —O <sub>12</sub>		1.351	—18.1	1.367	—16.5
O <sub>12</sub> ...H <sub>13</sub>		0.949	—14.0	0.971	—12.8
O <sub>7</sub> ...O <sub>12</sub>		2.704	0.5	2.548	0.4
C <sub>4</sub> —C <sub>5</sub>		1.495	—16.0	1.474	—15.6
C <sub>10</sub> —C <sub>11</sub>		1.446	—18.3	1.427	—17.9
C <sub>2</sub> —C <sub>3</sub>		1.452	—18.4	1.426	—17.9
C <sub>5</sub> =C <sub>6</sub>		1.349	—22.5	1.343	—22.8
C <sub>9</sub> =C <sub>10</sub>		1.374	—21.9	1.368	—21.1
C <sub>1</sub> —C <sub>2</sub>		1.451	—18.2	1.430	—17.7
C <sub>2</sub> —C <sub>8</sub>		1.436	—19.3	1.418	—18.6
C <sub>1</sub> —C <sub>6</sub>		1.470	—16.6	1.449	—16.1
C <sub>8</sub> —C <sub>9</sub>		1.438	—18.2	1.423	—17.7
C <sub>1</sub> —C <sub>14</sub>		1.395	—21.0	1.385	—20.3
C <sub>8</sub> —C <sub>16</sub>		1.431	—18.6	1.417	—18.0
C <sub>14</sub> —C <sub>15</sub>		1.421	—18.9	1.409	—18.4
C <sub>15</sub> =C <sub>16</sub>		1.384	—21.3	1.378	—20.6
C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>		117.1°	—	116.4°	—
C <sub>4</sub> —C <sub>3</sub> —C <sub>11</sub>		123.4°	—	121.4°	—
C <sub>3</sub> —C <sub>11</sub> —C <sub>10</sub>		121.0°	—	121.2°	—

Table III (contd.)

Molecule	Atomic pairs	MNDO		AM1	
		Distance or angle	$E_{AB}$	Distance or angle	$E_{AB}$
	C <sub>3</sub> —C <sub>4</sub> —O <sub>7</sub>	123.4°	—	122.7°	—
	C <sub>3</sub> —C <sub>11</sub> —O <sub>12</sub>	119.4°	—	118.1°	—
	C <sub>11</sub> —O <sub>12</sub> —C <sub>13</sub>	113.5°	—	108.2°	—
	C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	122.5°	—	122.3°	—
	C <sub>9</sub> —C <sub>10</sub> —C <sub>11</sub>	119.5°	—	119.8°	—
	C <sub>1</sub> —C <sub>2</sub> —C <sub>8</sub>	117.4°	—	118.9°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	118.5°	—	120.0°	—
6	C <sub>3</sub> —C <sub>4</sub>	1.506	—16.0	1.477	—15.5
	C <sub>3</sub> —C <sub>11</sub>	1.407	—21.1	1.389	—20.3
	C <sub>4</sub> =O <sub>7</sub>	1.229	—26.8	1.239	—25.3
	C <sub>11</sub> —O <sub>12</sub>	1.364	—17.3	1.381	—15.8
	O <sub>12</sub> . . . H <sub>13</sub>	0.950	—14.0	0.969	—12.7
	O <sub>7</sub> . . . O <sub>12</sub>	2.761	0.5	2.598	0.4
	C <sub>4</sub> —C <sub>5</sub>	1.494	—16.0	1.472	—15.6
	C <sub>10</sub> —C <sub>11</sub>	1.446	—18.2	1.425	—17.9
	C <sub>2</sub> —C <sub>3</sub>	1.454	—18.2	1.428	—17.8
	C <sub>5</sub> =C <sub>6</sub>	1.350	—23.5	1.343	—22.8
	C <sub>9</sub> =C <sub>10</sub>	1.375	—21.8	1.370	—21.0
	C <sub>1</sub> —C <sub>2</sub>	1.451	—18.2	1.429	—17.7
	C <sub>2</sub> —C <sub>8</sub>	1.433	—19.4	1.418	—18.6
	C <sub>1</sub> —C <sub>6</sub>	1.467	—16.7	1.449	—16.1
	C <sub>8</sub> —C <sub>9</sub>	1.439	—18.2	1.422	—17.7
	C <sub>1</sub> —C <sub>14</sub>	1.395	—21.0	1.384	—20.3
	C <sub>8</sub> —C <sub>16</sub>	1.435	—18.5	1.418	—17.9
	C <sub>14</sub> —C <sub>15</sub>	1.422	—18.8	1.411	—18.3
	C <sub>15</sub> =C <sub>16</sub>	1.383	—21.3	1.376	—20.7
	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	117.1°	—	116.7°	—
	C <sub>4</sub> —C <sub>3</sub> —C <sub>11</sub>	123.2°	—	121.3°	—
	C <sub>3</sub> —C <sub>11</sub> —C <sub>10</sub>	121.0°	—	121.4°	—
	C <sub>3</sub> —C <sub>4</sub> —O <sub>7</sub>	123.0°	—	122.1°	—
	C <sub>3</sub> —C <sub>11</sub> —O <sub>12</sub>	123.6°	—	120.1°	—
	C <sub>11</sub> —O <sub>12</sub> —H <sub>13</sub>	112.1°	—	106.5°	—
	C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	122.4°	—	122.2°	—
	C <sub>9</sub> —C <sub>10</sub> —C <sub>11</sub>	120.3°	—	119.6°	—
	C <sub>1</sub> —C <sub>2</sub> —C <sub>8</sub>	118.3°	—	119.3°	—
	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	118.5°	—	119.7°	—

Further, the AM1 method gives a reasonable prediction of O . . . O shortening in symmetrical transition structures 2 and 4. The MNDO approach gives a similar result for 4 but fails in 2, probably due to intrinsic imperfections. If we apply the generally adopted criterion for classification of hydrogen bonds<sup>24</sup> to distances estimated by the AM1 method, then one can say that the intramolecular H-bond in 1 belongs to the bonds of medium strength, whereas system 3 possesses a strong hydrogen bond. Is it possible to corroborate this distinction by semiempirical theory? The answer is negative because the difference in total energy  $E(1a) - E(1)$  is about 10 kcal mol<sup>-1</sup>, which is by 3 kcal mol<sup>-1</sup> higher than  $E(5) - E(3)$ . We don't believe that this

<sup>a</sup> X-ray structure of Ref. (3).

is a consequence of failure of the AM1 approach. Rather, we feel that the bridgehead O...O distance is perhaps a good criterion for intermolecular H-bonds but it should not be used in measuring strength of intramolecular hydrogen bonding. One could argue that in *1a* hydrogen atoms H<sub>8</sub> and H<sub>9</sub> have a close contact and a high nonbonding interaction (0.236 eV) whereas H<sub>13</sub> and H<sub>23</sub> atoms in *5* are more distant with concomitant matrix element of 0.121 eV. Their difference makes 2.7 kcal mol<sup>-1</sup> which would make hydrogen-bond strengths in *1* and *3* more alike (5 kcal/mol and 4.4 kcal/mol for *1* and *3*, respectively, if the nonbonded interactions (H<sub>8</sub>...H<sub>9</sub> and H<sub>13</sub>...H<sub>23</sub>) in *trans*-forms *1a* and *5* are neglected. In fact, their omitting is fully justified because they have nothing to do with intramolecular H-bonding. But even in this case hydroxyphenalenone does not have a stronger H-bond than hydroxy-formylfulvene.

Perusal of structural data in Table III reveals a pronounced localization in *3*, as schematically shown in Figure 2. However, bonds C<sub>3</sub>C<sub>11</sub> and C<sub>2</sub>C<sub>8</sub> are less localized as it might be inferred from the valence bond structure presented in Figure 2. They are longer than other double bonds in a molecule. Therefore, it seems that some delocalization is present in the central part of the carbon skeleton. A substantial increase in delocalization is found in symmetric form *4* as expected.

Comparison with the X-ray data of Haddon *et al.*<sup>3</sup> is very interesting. Theoretical structure of *3* is in excellent disagreement with the solid state measured values (Table III). Surprisingly enough, the experiment is in much better accordance with the symmetrical structure C<sub>2v</sub> (*4*), in particular with the AM1 results, in spite of some asymmetry in proton position and some difference in bond distances of the corresponding bonds leading to C<sub>s</sub> symmetry. It is possible that gas- and crystal-phase structures are different. More experimental and theoretical work is needed here.

We shall briefly discuss the results of the energy partitioning for 9-hydroxyphenalenone systems as obtained by the AM1 method. The changes in energy components in *3* and *5* follow the same pattern as in 6-hydroxy-2-formylfulvene (*vide supra*) although the actual numbers somewhat differ in magnitude. But, again the *trans*-form *5* has lower one-center total energy and increased non-bonded repulsions. On the other hand, the ground state conformer *3* has lower two-center bonding interactions:

$$E(5) - E(3): \quad \frac{E_2^t(\text{b})}{0.33} \quad \frac{E_2^t(\text{nb})}{0.22} \quad \frac{E_1^t}{-0.24}$$

It is interesting to point out that the difference in E<sub>2</sub><sup>t</sup>(nb) is substantially smaller than in *1* and *1a* systems. One of the reasons is that H<sub>8</sub>...H<sub>9</sub> atoms do not have such a close contact in *5* as it is the case in *1a* (*vide supra*). The term describing the interaction between H<sub>13</sub> and O<sub>7</sub> is -0.937 eV and -0.254 eV in *3* and *5*, respectively, thus making the largest portion of the relative difference in stability. This amount is diminished by the one-center stabilization of the *trans*-form *5*.

Analysis of the energy components in *3* and in symmetric arrangement of H<sub>13</sub> atom and of other equivalent bonds (*4*) is instructive. They are as follows (in eV):

$$E(4) - E(3): \quad \frac{E_2^t(\text{b})}{-0.67} \quad \frac{E_2^t(\text{nb})}{1.18} \quad \frac{E_1^t}{0.66}$$

Note that all interactions along the bridge O...H—O and O...H...O are again considered as bonding. Comparison with 6-hydroxy-2-formylfylvne reveals only a qualitative similarity. One observes a substantial increase in nonbonded repulsions in the symmetric form 4. This is the main reason why the barrier height for proton tunneling in 3 is higher than that in 1 (by 11 kcal mol<sup>-1</sup>).

TABLE IV

Formal atomic charges and molecular dipole moments in 6-hydroxy-2-formylfylvne systems 1, 1a and 2, as calculated by MNDO and AM1 methods (in |e| and Debys, respectively)\*

Atom	1	1a	2
C <sub>1</sub>	-0.21(-0.19)	-0.17(-0.16)	-0.29(-0.28)
C <sub>2</sub>	-0.07 (0.00)	-0.09(-0.01)	0.04(-0.04)
C <sub>5</sub>	-0.21(-0.20)	-0.14(-0.14)	-0.29(-0.28)
C <sub>6</sub>	0.14 (0.24)	0.09 (0.19)	0.37 (0.26)
C <sub>10</sub>	0.25 (0.33)	0.23 (0.31)	0.37 (0.26)
O <sub>7</sub>	-0.24(-0.24)	-0.19(-0.21)	-0.36(-0.35)
O <sub>11</sub>	-0.34(-0.34)	-0.28(-0.29)	-0.36(-0.35)
H <sub>8</sub>	0.27 (0.24)	0.22 (0.20)	0.33 (0.35)
C <sub>4</sub>	-0.09(-0.02)	-0.12(-0.05)	0.04(-0.04)
C <sub>3</sub>	-0.19(-0.12)	-0.17(-0.11)	-0.17(-0.23)
H <sub>9</sub>	0.17 (0.09)	0.13 (0.05)	0.06 (0.14)
H <sub>12</sub>	0.09 (0.01)	0.08(-0.00)	0.06 (0.14)
H <sub>13</sub>	0.14 (0.07)	0.14 (0.07)	0.06 (0.14)
H <sub>15</sub>	0.14 (0.07)	0.14 (0.06)	0.06 (0.14)
H <sub>14</sub>	0.15 (0.08)	0.15 (0.08)	0.07 (0.14)
	Molecular dipole moments		
$\mu$	2.22 (1.95)	2.99 (2.99)	0.91 (1.45)

\* MNDO values are given in parentheses.

Charge (atomic) distributions and dipole moments are presented in Tables IV and V. Rotation of O<sub>7</sub>—H<sub>8</sub> bond of the H-bridge in 1 to *trans* position (1a) by 180° causes a moderate redistribution of electron density. Noteworthy changes take place on the hydrogen bridge O<sub>11</sub>...H<sub>8</sub>—O<sub>7</sub> and the fragment which carries the bridge: C<sub>10</sub>—C<sub>1</sub>—C<sub>5</sub>=C<sub>6</sub>. In contrast, substantial changes in formal atomic charges are found in symmetric form 2 in accordance with the delocalized nature of this system. A dramatic decrease in electron density takes place on sites C<sub>6</sub> and C<sub>10</sub>. We would like to recall in passing that an increase in one-center energy of these atoms relative to 1 is one of the reasons why the symmetric hydrogen bond is less stable. This simple rule of thumb has a general validity in a qualitative sense: the more electron density on the atom — the lower its single-center energy. The hydrogen in the symmetric position has lower electron density and higher intrinsic atomic energy concomitant with earlier energetic consideration. It is interesting to notice that the asymmetric (C<sub>s</sub>) form has an appreciable higher dipole moment than symmetric H-bond (C<sub>2v</sub>).

TABLE V

Formal atomic charges and molecular dipole moments in 9-hydroxyphenalenone systems 3–6, as calculated by MNDO and AM1 methods (in  $|e|$  and Debye, respectively)\*

Atom	3	4	5	6
C <sub>4</sub>	0.31 (0.32)	0.31 (0.35)	0.30 (0.31)	0.29 (0.30)
C <sub>3</sub>	-0.25(-0.25)	-0.35(-0.38)	-0.19(-0.18)	-0.17(-0.16)
C <sub>11</sub>	0.20 (0.24)	0.30 (0.35)	0.16 (0.20)	0.14 (0.17)
O <sub>7</sub>	-0.36(-0.35)	-0.36(-0.36)	-0.28(-0.29)	-0.28(-0.29)
H <sub>13</sub>	0.27 (0.23)	0.36 (0.32)	0.22 (0.20)	0.23 (0.20)
O <sub>12</sub>	-0.25(-0.25)	-0.37(-0.36)	-0.20(-0.22)	-0.26(-0.27)
C <sub>5</sub>	-0.22(-0.14)	-0.20(-0.15)	-0.21(-0.13)	-0.21(-0.14)
C <sub>6</sub>	-0.05 (0.02)	-0.02 (0.06)	-0.07(-0.00)	-0.06(-0.00)
C <sub>10</sub>	-0.18(-0.11)	-0.23(-0.15)	-0.22(-0.16)	-0.17(-0.10)
C <sub>1</sub>	-0.08(-0.09)	-0.13(-0.13)	-0.07(-0.08)	-0.07(-0.07)
C <sub>2</sub>	0.05 (0.06)	0.08 (0.11)	0.04 (0.05)	0.02 (0.03)
C <sub>8</sub>	-0.09(-0.10)	-0.10(-0.13)	-0.09(-0.10)	-0.07(-0.07)
C <sub>9</sub>	-0.05 (0.02)	-0.02 (0.06)	-0.04 (0.04)	-0.07 (0.01)
C <sub>14</sub>	-0.07 (0.01)	-0.05 (0.04)	-0.08 (0.01)	-0.08 (0.00)
C <sub>15</sub>	-0.16(-0.09)	-0.18(-0.12)	-0.15(-0.09)	-0.14(-0.08)
H <sub>17</sub>	0.16 (0.08)	0.16 (0.08)	0.15 (0.20)	0.15 (0.20)
H <sub>18</sub>	0.14 (0.06)	0.14 (0.06)	0.13 (0.08)	0.14 (0.08)
H <sub>19</sub>	0.14 (0.06)	0.13 (0.06)	0.14 (0.06)	0.14 (0.06)
H <sub>20</sub>	0.14 (0.07)	0.14 (0.07)	0.14 (0.07)	0.14 (0.07)
Molecular dipole moments				
$\mu$	3.98 (3.41)	4.27 (3.87)	4.57 (4.33)	4.73 (4.44)

\* MNDO values are given in parentheses.

9-Hydroxyphenalenone systems in many respect follow the pattern of 6-hydroxy-2-formylfulvene regarding atomic charges but there is also *differentia specifica*. Atom C<sub>3</sub> in 3 takes the role of atoms C<sub>1</sub> and C<sub>5</sub> in 1. Hence, it attracts additional electron charge density in symmetric form 4. Carbon atoms carrying O...H...O bridge, on the contrary, lose some density but the effect is less pronounced than in 1a. On the other hand H<sub>13</sub> atom has a higher positive charge in 4 than H<sub>3</sub> in 1a. Hence, we conclude that asymmetric O...H—O and symmetric O...H...O intramolecular hydrogen bonds have some common general characteristics in quite different molecular systems although there are quantitative differences. Finally, it should be mentioned that 3 has a smaller dipole moment than 4.

#### CONCLUSION

The present results provide additional evidence that semiempirical MINDO/3, MNDO and AM1 methods are useful in discussing the properties of compounds possessing intramolecular hydrogen bonds. The former two methods usually provide information at the qualitative level whilst the latter is capable of giving semiquantitative results after some empirical adjustment(s). Our results show that in both systems, 1 and 3, asymmetrical H-bond is more stable than the symmetrical one in agreement with gas-phase ESCA spectra<sup>14</sup> and quadrupole coupling constants measurements<sup>15</sup>. They also indicate

that the H-bond strength is slightly higher in 6-hydroxy-2-formylfulvene than in 9-hydroxyphenalenone. Interestingly, the barrier height for proton tunnelling is higher in 9-HPO than in 1. The barrier of O—H out of plane rotation in 9-HPO is 9 kcal mol<sup>-1</sup>. Finally, relative stabilities of symmetric vs. asymmetric H-bond systems are interpreted in terms of energy components obtained by the energy partitioning technique.

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## REFERENCES

1. Z. B. Maksić, M. Eckert-Maksić, and D. Kovaček, *Croat. Chem. Acta* **62** (1989) 623 and the references cited therein.
2. H. Fuess and H. J. Lindner, *Chem. Ber.* **108** (1975) 3096.
3. S. Svensson, S. C. Abrahams, J. L. Bernstein, and R. C. Haddon, *J. Amer. Chem. Soc.* **101** (1979) 5759.
4. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.* **97** (1975) 1285.
5. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.* **99** (1977) 4899.
6. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Amer. Chem. Soc.* **107** (1985) 3902.
7. T. J. Zielinski, D. L. Breen, and R. Rein, *J. Amer. Chem. Soc.* **100** (1978) 6266.
8. G. Klopman, P. Andreozzi, A. J. Hopfinger, O. Kikuchi, and M. J. S. Dewar, *J. Amer. Chem. Soc.* **100** (1978) 6286.
9. M. J. S. Dewar and H. S. Rzepa, *J. Amer. Chem. Soc.* **100** (1978) 58; S. Schneider, *Theoret. Chim. Acta* **57** (1980) 71.
10. M. Eckert-Maksić, P. Bischof, and Z. B. Maksić, *Croat. Chem. Acta* **58** (1985) 407; *J. Mol. Structure Theochem* **139** (1986) 1315.
11. M. Eckert-Maksić, and Lj. Maksimović, *Croat. Chem. Acta* **59** (1986) 757; *J. Mol. Structure Theochem* **153** (1987) 121.
12. K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schulz, *Chem. Ber.* **97** (1964) 2066.
13. H. M. Pickett, *J. Amer. Chem. Soc.* **95** (1973) 1770.
14. R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *J. Amer. Chem. Soc.* **101** (1979) 3157.
15. L. M. Jackman, J. C. Trewella, and R. C. Haddon, *J. Amer. Chem. Soc.* **102** (1980) 2519.
16. Y. Demura, T. Kawato, H. Kanatomi, and I. Murase, *Bull. Chem. Soc. Japan* **48** (1975) 2820.
17. G. Karlström, B. Jönsson, B. Roos, and H. Wennerström, *J. Amer. Chem. Soc.* **98** (1976) 6851.
18. P. George, C. W. Bock, and M. Trachtman, *J. Comp. Chem.* **1** (1980) 373.
19. H. Fischer and H. Kollmar, *Theoret. Chim. Acta* **16** (1970) 163.
20. M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.* **93** (1971) 7201; M. J. S. Dewar, D. H. Lo, and Z. B. Maksić, *Croat. Chem. Acta* **46** (1974) 7.
21. J. B. Moffat, *Croat. Chem. Acta* **57** (1984) 1475 and the references cited therein.
22. J. Bicerano, H. F. Schaefer III, and W. H. Miller, *J. Amer. Chem. Soc.* **105** (1983) 2550.
23. W. F. Rowe, Jr., R. W. Duerst, and E. B. Wilson, *J. Amer. Chem. Soc.* **98** (1976) 4021; S. L. Baugheum, R. W. Duerst, W. F. Rowe, Z. Smith, and E. B. Wilson, *J. Amer. Chem. Soc.* **103** (1981) 6296.
24. J. Emsley, *Structure and Bonding*, Springer, Verlag Heidelberg, **57** (1984) 148.

## SAŽETAK

## Semiempirijski studij intramolekularne vodikove veze u 6-hidroksi-2-formilfulvenu i 9-hidroksifenalenonu

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Primjenom semiempirijskih metoda MINDO/3, MNDO and AM1 ustanovljeno je da su intramolekularne veze u molekulama 6-H-2-FF i 9-HPO asimetrične. Relativne stabilnosti razmatrane su i interpretirane primjenom tehnike particije ukupne energije.