Symmetrical Hydrogen Bonding: Molecular Orbital Theory of the π-Electron Component

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Abstract: A molecular orbital theory of the intrinsic ability of functional groups to develop symmetrical hydrogen bonding is presented. The treatment is based on the second-order Jahn–Teller effect, and is developed at both qualitative and quantitative levels of approximation. A variety of molecules is examined, and the results of the theory are shown to be in good agreement with the available experimental evidence.

The hydrogen bond plays a crucial role in many aspects of chemistry,[1-10] Theoretical analysis has intensified in recent years,[7-10] but the decomposition of contributions to the energy of the hydrogen bond remains essentially unchanged from the original Coulson scheme[11,12] (electrostatic, delocalization, dispersive, and repulsive forces). Our knowledge of the details of hydrogen bonding has been enhanced by the publication of a number of sophisticated quantum-chemical treatments of the subject.[7-26]

The present study focuses on hydrogen bonds which have the *potentiality* for being symmetric (at least C_{2v} symmetry) but in fact our remarks apply in a qualitative sense to all hydrogen-bonding situations. The approach is entirely distinct from previous treatments. We take no account of the stereochemical relationship of the receptor atoms[27] or the σ-bond system involved in the hydrogen bond (**1**), but rather we focus on the *intrinsic ability of the structural unit to develop hydrogen bonding* (for which the symmetric situation **1b** repre-

1a **1b**

sents the limiting case). The analysis is effected by an examination of the tendency of the molecular framework (to which the hydrogen atom is attached) toward asymmetry. The π-electron skeleton and the hydrogen-bond system are assumed to be rigidly coupled so that asymmetry in one component necessarily scales with asymmetry in the other (and vice versa).

It is the purpose of this paper to show that the electronic system which is coupled to the receptor atoms[27] (X) in a hydrogen bond (**1**) exerts a powerful influence on the strength of the hydrogen bond, and indeed determines the final symmetry.

Theory

Qualitative Treatment. Orbital Interactions. For concreteness we consider the intramolecular hydrogen bond present in the β-keto enol unit (**2**), since this system has received the most attention.[19,20,22,23,26,28-50]

2a (C_s) **2b** (C_{2v})

The highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) for **2b** are shown schematically in Figure 1. The symmetries are B_1 and A_2, respectively, and the transition moment (direct product) is therefore of B_2 symmetry which carries **2b** into **2a.** Thus we can consider the distortion of **2b** to **2a** as a second-order Jahn–Teller effect,[51-61] Furthermore, as configuration interaction between the HOMO and LUMO is the dominant effect in such cases, we can obtain most of the information we require (in a qualitative sense) from a consideration of these two orbitals. In particular, we shall be concerned with the way in which the HOMO–LUMO energy gap ($\Delta E = \epsilon_{LUMO} - \epsilon_{HOMO}$) responds to changes in the electronic structure of **2** as a result of variations in functionality. Clearly the ease of distortion will bear an inverse relationship to the magnitude of the energy gap (ΔE) (see below).

Figures 2 and 3 summarize the effects of symmetrical substitution patterns on ΔE in **2b.** It may be seen that substitution at the 2,4 positions (Figure 2) leads to an increase in ΔE for electron-donating substituents and a decrease in ΔE for electron-accepting substituents. The inverse situation applies in the case of substitution at the 3 position (Figure 3), where electron-donating substituents decrease ΔE and electron-accepting substituents increase ΔE.

These orbital interaction diagrams follow from the coefficients and particularly the nodal properties of the wave functions[62] given in Figure 1. Thus substitution at the 3 position has no effect (to first order) on the LUMO but a large effect on the HOMO, whereas substitution at the 2,4 positions has a very small effect on the HOMO but a large effect on the LUMO. Thus the two substitution schemes play complementary roles in their interaction with both the HOMO and the LUMO of **2b.**

The effect of the electronegativity of the receptor atom may be treated in similar fashion (Figure 4) via the Coulomb integral (α). Thus in the β-keto enol case, where the coefficients of the HOMO at the hydrogen bond receptor atom are larger in magnitude than those of the LUMO,[62] an increase in the electronegativity ($\delta\alpha$ positive) will serve to increase the energy gap and thereby stabilize form **2b** and strengthen the hydrogen bond (and vice versa). In fact the change in the energy gap ($\delta\Delta E$) may be obtained from $\delta\Delta E = 2(c^2_{HOMO,X} - c^2_{LUMO,X})\delta\alpha_X$ (to first order).[63]

Quantitative Treatment. Eigenvalues and Eigenvectors of Bond–Bond Polarizability Matrix $\pi_{rs,tu}$. The preceding qualitative theory allows the satisfactory treatment of many hydrogen bonding situations that have the potentiality to be symmetric. In cases where the hydrogen bond receptor atoms (X) in **1** are bonded to complex electronic systems the simple analysis presented above is difficult to apply and a more rigorous and quantitative theory becomes desirable.

We propose that such a theoretical level may be provided by diagonalization of the bond–bond polarizability matrix ($\pi_{rs,tu}$) for **1b.** The eigenvalues of this matrix provide a mea-

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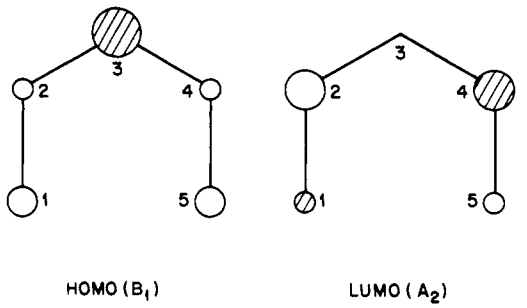


Figure 1. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for malonaldehyde[62] (**2b**/**3a**).

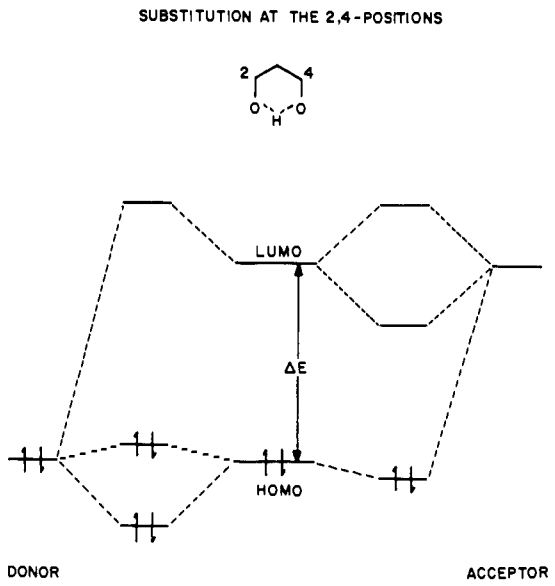


Figure. 2. Orbital interaction diagram in the case of substitution at the 2,4 positions of **2b**/**3a**.

sure of the energy gain accompanying distortions, whereas the eigenvectors indicate the symmetry,[53,64-66] We are therefore required to solve

$$\| \pi_{rs,tu} - \lambda_{rs}\delta_{rs,tu} \| = 0 \qquad (1)$$

where

$$\pi_{rs,tu} = 2 \sum_{k}^{\text{occ}} \sum_{l}^{\text{unocc}} \frac{(c^*_{kr}c_{ls} + c^*_{ks}c_{lr})(c_{kt}c^*_{lu} + c_{ku}c^*_{lt})\beta^{-1}}{(\epsilon_k - \epsilon_l)} \qquad (2)$$

and c_{kr} is the coefficient of MO k at atom r and ϵ_k is the energy of MO k.

We have found that it is quite sufficient to solve these equations at the HMO level of approximation (for **1b**), employing an average of the parameters appropriate to the distorted form (**1a**).

The eigenvalues obtained from eq 1 provide a measure of the force constant for distortion from a symmetrical hydrogen bond (large values indicate a favorable distortion), Matched against this will be the restoring forces from the non-π-electron components of the molecule. It should be noted that these forces will be different for each set of receptor atoms (X in **1**) and each distinct stereochemical relationship of the receptor atoms. Only experience will lead to a critical value for λ (λ_{crit}) in any given case, that is, a value of λ below which hydrogen bonds are stable to distortion and remain symmetrical. Given the fact that many asymmetrical hydrogen bonding situations do not lie very far along the distortion coordinate from the symmetrical form (that is, the geometry of **1a** is not very different from that of **1b**), we might expect that *the eigenvalue* (λ) *provides a measure of the degree of distortion or asymmetry*. This corresponds to using Hooke's law for displacements along a transition-state coordinate. Reference to the eigenvectors allows us to determine whether a distortion eigenvalue is antisymmetric with respect to the bonds to the receptor atoms (and thus coupled to asymmetry in the hydrogen bond). The results for malonaldehyde (**3a**) (Table I) exemplify the treatment.

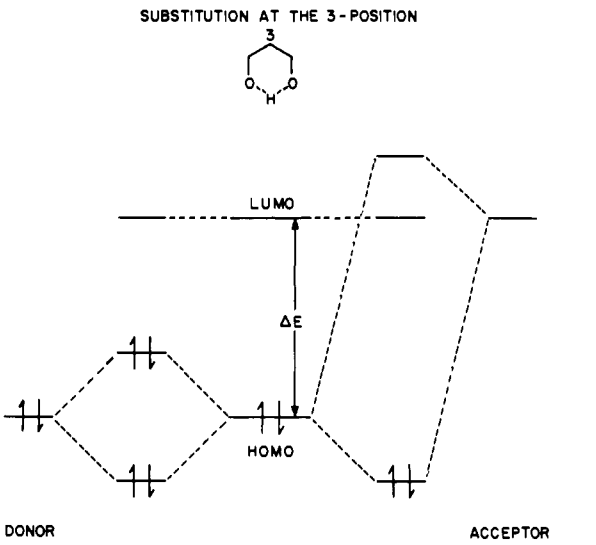


Figure 3. Orbital interaction diagram in the case of substitution at the 3 position of **2b**/**3a**.

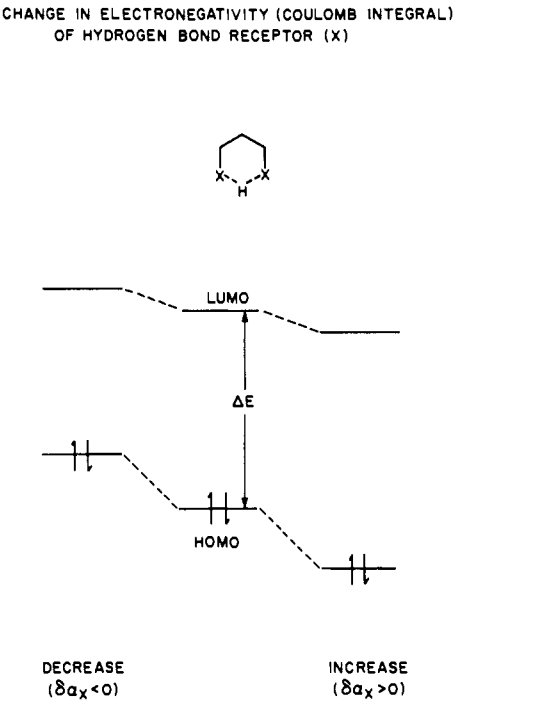


Figure 4. Orbital interaction diagram for change in electronegativity of receptor atom of **2b**.

Results and Discussion

In comparing our calculations of hydrogen-bond strength (eigenvalues, λ) with experiment we shall make use of diffraction measurements of the X- - -X separation (Table II). Experience has shown that the O–H bond length has an inverse relationship to the O- - -O distance in OHO hydrogen bond situations.[50,67] That is, the O- - -O separation provides a measure of the tendency of the O–H bond length to expand to the symmetrical configuration O- -H- -O (**1b**, X = O).

Table I. Eigenvalues and Eigenvectors of the Bond–Bond Polarizability Matrix ($\pi_{rs,tu}$) of Malonaldehyde (**3a**)

	1	2	3	4
$\lambda(\beta^{-1})$	1.067	0.337	0.142	0.022
bond r–s				
1-2	0.467	0.676	−0.531	0.208
2-3	−0.531	−0.208	−0.467	0.676
3-4	0.531	−0.208	0.467	0.676
4-5	−0.467	0.676	0.531	0.208
symmetry	B_2	A_1	B_2	A_1

Table II. Experimental Hydrogen Bond Receptor Atom Separations (**1**)

compd	X	X- - -X, Å	ref
3a	O	2.555	28
3 (R_1 = CF_3; R_2 = H)	O	2.551	29
3j	O	2.519	30
3g	O	2.463	32
4	O	2.40, 2.41	33
3q	O	2.384	34
5	O	2.486	35
6	O	2.574, 2.576, 2.619	36
7	O	2.553	37
8a	O	2.513, 2.550	38
9	$O^{-1/2}$	2.44	39
19b	N	2.51	42
20b	N	2.79	43

As might be expected, other experimental quantities correlate with the eigenvalues of our treatment, but these results will be reported elsewhere.

β-Keto Enols (2–6). The eigenvalues collected in the first part of Table I bear out the preceding remarks regarding substituent effects on the hydrogen bonding in β-keto enols. The substituent effects follow the Hammett scheme (within the qualitative treatment), with the exception of the cyano group. It is possible that this is a real effect but it seems more likely to be an artifact of the parametrization scheme (see Calculational Section). Reference to Table I shows that the phenyl group is predicted to favor a symmetrical skeleton and enhance hydrogen bonding in all modes of substitution.

The regression analysis between the eigenvalues and the experimental O- - -O separations of β-keto enols for which structures are available is shown in Figure 5. Note that only structures based on **3** are included in the analysis. Compounds with a β-keto enol unit fused to an aromatic ring system (**5** and **6**) are omitted because the rigidity in the backbone will lead to stiffer restoring forces than those present in **3**, thus damping their response to the π-electron component (Figure 5). In fact the diffraction study of **6** shows quite clearly that the oxygen atoms are canted away from one another, in agreement with our finding of a strongly favored distortional mode in this molecule. As expected, **6a** is preferred to **6b** for the distorted form.

It is interesting to note that nitromalonamide (**3q**) is found to have the lowest eigenvalue of distortion (this is also in agreement with Hammett considerations). The X-ray diffraction study[34] found a very short O- - -O separation (2.384 (4) Å), well in the range for a symmetrical hydrogen bond, but the authors concluded that **3q** has O–H distances of 1.01 (5) and 1.44 (5) Å. Such a result would be in serious disagreement with the Nakomoto, Margoshes, and Rundle correlation,[50,67] and the compound clearly merits further attention. Our results do indicate (Table III) that, if **3q** does not possess a symmetrical hydrogen bond, such a condition is not likely to occur in other simple derivatives of **3**. Usnic acid (**4**) is another molecule with a short O- - -O separation,[33] in good agreement with the qualitative treatment (donor groups at the 2 and 4 positions and an acceptor group at the 3 position of **3**).

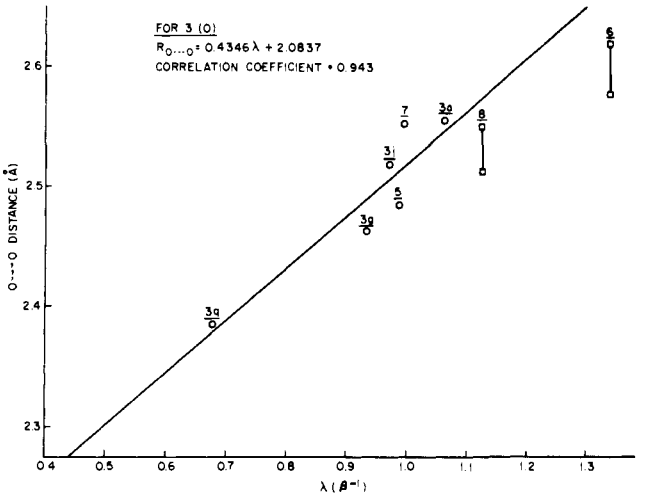
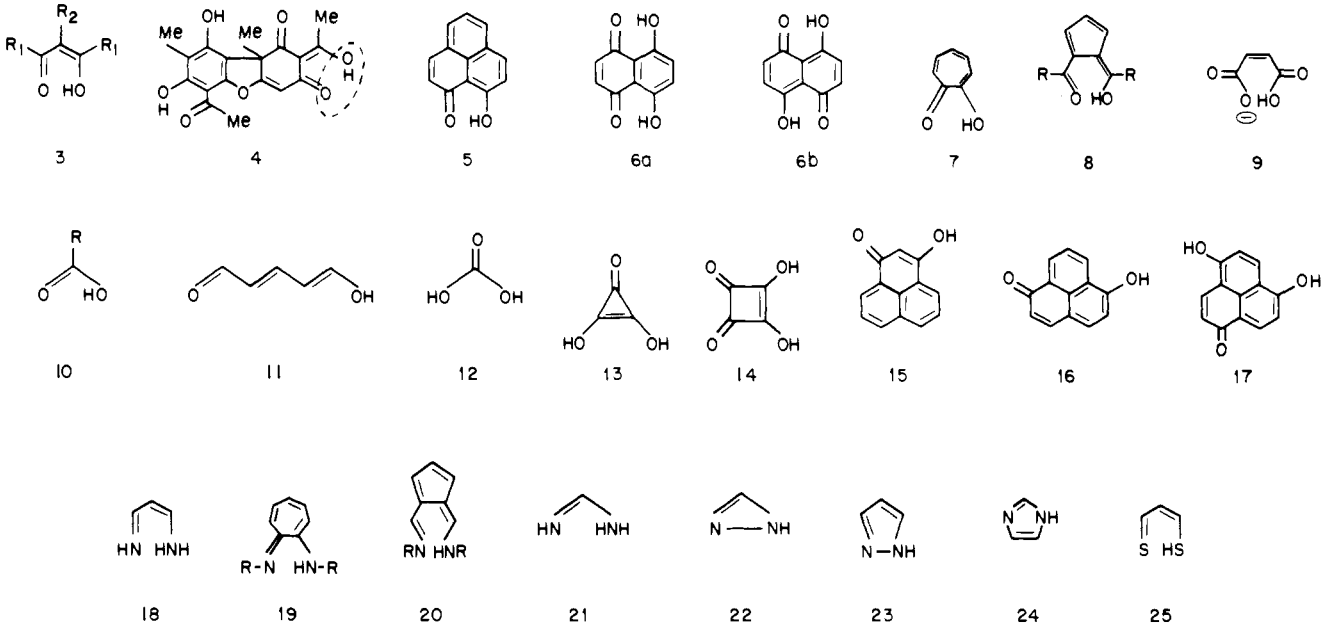


Figure 5. Regression of calculated λ values against experimental O- - -O separations. Note that only the unconstrained β-keto enols (O) are included in the analysis.

Table III. Eigenvalues (λ) and Symmetry

				symmetry	
compd	R_1	R_2	λ	initial	distortion
3a	H	H	1.067	C_{2v}	B_2
3b	HC=O	H	1.114	C_{2v}	B_2
3c	H	HC=O	0.875	C_{2v}	B_2
3d	RO	H	0.942	C_{2v}	B_2
3e	H	RO	1.152	C_{2v}	B_2
3f	RO	HC=O	0.833	C_{2v}	B_2
3g	Ph	H	0.933	C_{2v}	B_2
3h	H	Ph	1.016	C_{2v}	B_2
3i	Ph	HC=O	0.757	C_{2v}	B_2
3j	Me	H	0.972	C_{2v}	B_2
3k	CN	H	1.061	C_{2v}	B_2
3l	H	CN	0.982	C_{2v}	B_2
3m	NO_2	H	1.027	C_{2v}	B_2
3n	H	NO_2	0.869	C_{2v}	B_2
3o	NR_2	H	0.931	C_{2v}	B_2
3p	H	NR_2	1.172	C_{2v}	B_2
3q	NR_2	NO_2	0.678	C_{2v}	B_2
5			0.989	C_{2v}	B_2
6a			1.343	D_{2h}	B_{2u}
6b			0.769	D_{2h}	B_{1g}
7			1.012	C_{2v}	B_2
8a	H		1.128	C_{2v}	B_2
8b	Ph		1.047	C_{2v}	B_2
9			0.499	C_{2v}	B_2
10a	H		0.625	C_{2v}	B_2
10b	Ph		0.562	C_{2v}	B_2
11			1.333	C_{2v}	B_2
12			0.530	D_{3h}	E′
13			0.608	D_{3h}	E′
14			0.924	D_{2h}	B_{2u}
15			0.942	C_{2v}	B_2
16			1.071	C_{2v}	B_2
17			0.915	C_{3h}	E′
18			1.097	C_{2v}	B_2
19a	H		1.115	C_{2v}	B_2
19b	Me		1.175	C_{2v}	B_2
20a	H		1.070	C_{2v}	B_2
20b	Ph		1.054	C_{2v}	B_2
21			0.667	C_{2v}	B_2
22			2.155	C_{2v}	B_2
23			0.711	C_{2v}	B_2
24			0.448	C_{2v}	B_2
25			1.316	C_{2v}	B_2



α- and γ-Keto Enols (7, 8). Both tropolone (**7**)[37,45,47] and 6-hydroxy-2-formylfulvene (**8**)[38,45,47,68] have received considerable attention. This interest was apparently motivated by the hope that they might be symmetric. Particularly in the case of **8**, where the stereochemistry is ideal, strong hydrogen bonding would be expected on the basis of "resonance" considerations. Experience has in fact shown that such effects often work in the opposite direction and our results indicate that **7** and **8** do not show pronounced tendencies toward symmetrical structures and therefore do not possess intrinsically strong hydrogen bonds. The relatively long O- - -O distances (Table II) found for these compounds support this proposition.

Maleate Anion (9). In agreement with our finding that maleate anion (**9**) possesses the lowest λ value (at least in the present study), **9**[39] and a number of its derivatives[69] are known to possess short O- - -O distances with symmetric hydrogen bonds.

Intermolecular Hydrogen Bonds (10–17). There are a number of situations where the stereochemical relationship of the receptor atoms (X, **1**) is such that intramolecular hydrogen bonds are effectively precluded. In many of these cases intermolecular association via hydrogen-bond formation is known to occur. It is a simple matter to apply our treatment in this situation (subject to the requisite symmetry constraints), although it must be born in mind that the restoring forces in the case of intermolecular hydrogen bonding will be distinct from those present in the intramolecular case, owing to the extra degrees of freedom.

Turning first to the keto polyenol systems (**10a, 3a, 11**), we see that the propensity for strong hydrogen bonding decreases with increase in the chain length of the intervening π-electron segment. This effect, of course, has its origins in the reduction of the energy gap (ΔE) in such systems with the degree of conjugation. Thus we see that carboxylic acids[41] (**10**) have a strong intrinsic potential for hydrogen-bond formation (cf. the maleate anion (**9**)). It is clear from Table III that the intrinsically strongest hydrogen bonds are associated with small π-electron systems (for the same reason). A similar situation obtains in the case of ions such as FHF^- (which is known to be symmetric[2]), as the MOs are topologically equivalent to those of the carboxylic acid group (the importance of the electronegativity of the receptor atoms follows from our previous arguments).

The hydroxyphenalenones (**5, 15, 16**) show a similar trend. Both the β-hydroxy ketones (**5, 15**) are found to possess intrinsically stronger hydrogen bonds than the δ-hydroxy ketone **16.** Furthermore, **15** has a lower λ value than **5,** presumably because its β-hydroxy ketone hydrogen bond unit does not involve cross conjugation of a benzenoid ring system. The physical and chemical properties of these compounds indicate strong intramolecular hydrogen bondings for **5**[35,47,70–72] and strong intermolecular hydrogen bonding in the case of **15**[73] and **17.**[74]

Hydrogen Bond Receptor Atoms Other Than Oxygen (18–22). The λ values of some hydrogen-bonded systems with receptor atoms other than oxygen are given in the last part of Table III. In general the lower electronegativities of nitrogen and sulfur lead to intrinsically weaker hydrogen bonds than is the case with oxygen receptor atoms. This is not so for **8** and **20a.** As noted previously, the effect of changes in electronegativity of receptor atoms on hydrogen bond strength depends primarily on the magnitude of HOMO and LUMO coefficients at the hydrogen bond receptor. Normally the coefficients at the receptor atoms are larger in the HOMO than the LUMO and large electronegativity values therefore lead to strong hydrogen bonding. In the case of **8**/**20a** the relative magnitudes of the coefficients are reversed,[75] and a *decrease* in electronegativity is therefore predicted to increase the hydrogen-bond strength in this system.

Pyrazole[76] (**23**) and imidazole[24,77] (**24**) turn out be intrinsically strong hydrogen bonding systems, and there is a considerable body of experimental evidence to support this result. The **18**/**23** and **21**/**22** pairs provide an interesting perspective on the intrinsic hydrogen bonding potential of linear vis-à-vis cyclic conjugated systems. As expected from aromaticity considerations, hydrogen bonding is favored in cyclic systems for the 6π-electron case (**18**/**23**) and disfavored for the 4π-electron case (**21**/**22**).

Calculational Section

Most of the HMO parameters were taken from the compilation by Streitwieser.[78] The parameters for the cyano,[79] nitro,[80] and thio[72] groups were taken from ESR studies and may not be optimal for use in the present study. $\alpha_{\ddot{O}} = \alpha + 2.0\beta$, $\alpha_{\dot{O}} = \alpha + \beta$, $\alpha_{OH} = \alpha + 1.5\beta$, $\alpha_O{}^{NO_2} = \alpha + \beta$, $\alpha_{\dot{N}} = \alpha + 1.5\beta$, $\alpha_{\dot{N}} = \alpha + 0.5\beta$, $\alpha_{NH} = \alpha + \beta$, $\alpha_N{}^{C\equiv N} = \alpha + \beta$, $\alpha_N{}^{NO_2} = \alpha + 2.0\beta$, $\alpha_{SH} = \alpha + 0.5\beta$, $\alpha_C{}^{C-Me} = \alpha - 0.3\beta$, $\beta_{C-O} = \beta$, $\beta_{C-N} = \beta$, $\beta_{C-S} = 0.7\beta$, $\beta_{C-N}{}^{C\equiv N} = 2.0\beta$, $\beta_{N-O}{}^{NO_2} = \beta$.

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