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Role of Intermolecular Hydrogen Bonding in Some Supramolecules: An AM1 Study of the Binding Energies and Hyperpolarizabilities[1]

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Semiempirical calculations using the AM1 approximation to MO theory have been carried out on some donor and acceptor (DA) substituted aromatics containing carboxylic acid, amide, nitro···amino and nitro···dimethylamino hydrogen-bonded dimers. Intermolecular binding energies and molecular hyperpolarizabilities, β and γ, have been calculated. Hydrogen-bonding energies have not varied appreciably with the DA strengths in the acid and amide dimers; however, these energies increase in the other two dimers. These studies have also indicated that the hydrogen-bonding interactions in acid and amide dimers may not contribute to any significant enhancement of the hyperpolarizabilities, while the mutually induced polarization enhances the β value in the two nitro dimers. However the relative rise in γ is not so significant in all the four dimers. As there is no substantial charge transfer across the hydrogen bonds in these four dimers, the magnitude of β and γ is not in the order observed in stilbenes and tolans substituted with similar DA groups. Hydrogen bonding supplemented by a large mutual polarization could be useful in generating efficient second harmonic generating (SHG) materials based on supramolecules.

Introduction

Building supramolecules through molecular recognition characterized by intermolecular interactions has been suggested as a novel approach to design better nonlinear optical materials.[2] Of all the intermolecular interactions, hydrogen bonding is particularly important because of its varied nature with respect to the different groups involved in such a bonding.[3] Hyrogen bonding, particularly in the solid state, can be effectively used to tailor many materials with requisite physical and chemical properties.[4] The process of molecular recognition has been achieved by the optimization of O−H···O, N−H···O and C−H···O interactions involving a variety of functional groups.[5]

Hydrogen bonds have also been used in the possible generation of noncentrosymmetric structures, which is a prerequisite for an effective SHG crystal.[6] Although a few reports have appeared in the literature on the hyperpolarizabilities of some hydrogen-bonded (HB) systems, not much is known about the effects of various DA groups in these systems.[7] Thus, the relative strengths of some HB patterns and the effect of various DA groups on hydrogen bonding and hyperpolarizabilities have been studied here. Four HB patterns denoted by the motifs M1, M2, M3, and M4 and three non-hydrogen-bonded motifs, M5, M6, and M7 consisting of phenyl, stilbene, and tolan skeletons, respectively, are given in Figure 1. The $M_{\#}$ notation is intended to refer the different motifs. Each motif is para-disubstituted with one of the four donors ($D_{\#}$) and one of the six acceptors ($A_{\#}$) also shown in Figure 1.

Computational Methodology

In general, either centro (homodimer) or pseudocentrosymmetric (heterodimer) hydrogen-bonded dimers are observed in amide and acid crystals. Such a planar conformation is compatible in generating various packing patterns such as layers, ribbons, and tapes.[3,8] It was shown by Dannenberg that in the nitro···amino dimers, out of the many possible conformations, the linearly hydrogen-bonded conformation is the most stable.[9] Etter has also reported that such a conformation is

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Table 1. Hydrogen-Bonding Energies (kcal/mol) of DA-Substituted Heterodimers (Each Dimer Is in the Form of Donor−Motif−Acceptor)

		acceptors					
moiety	donor	$-COCH_3$	$-CHO$	$-CN$	$-COCl$	$-COCF_3$	$-NO_2$
amide dimer (M1)	$-OCH_3$	−7.98	−8.02	−8.11	−8.13	−8.20	−8.40
	$-NH_2$	−8.14	−8.18	−8.29	−8.32	−8.42	−8.51
	$-NHCH_3$	−8.13	−8.18	−8.29	−8.32	−8.42	−8.51
	$-N(CH_3)_2$	−8.14	−8.18	−8.29	−8.33	−8.43	−8.53
acid dimer (M2)	$-OCH_3$	−6.37	−6.38	−6.45	−6.47	−6.53	−6.56
	$-NH_2$	−6.40	−6.43	−6.51	−6.56	−6.53	−6.70
	$-NHCH_3$	−6.40	−6.43	−6.51	−6.56	−6.62	−6.70
	$-N(CH_3)_2$	−6.40	−6.43	−6.51	−6.56	−6.62	−6.70
amine···nitro dimer (M3)	$-OCH_3$	−5.35	−5.48	−5.60	−5.98	−6.27	−6.49
	$-NH_2$	−5.80	−5.93	−6.03	−6.51	−6.83	−7.08
	$-NHCH_3$	−5.83	−5.96	−6.11	−6.55	−6.88	−7.12
	$-N(CH_3)_2$	−5.86	−5.99	−6.11	−6.59	−6.86	−7.16
DiMe−amine···nitro dimer (M4)	$-OCH_3$	−1.21	−1.32	−1.42	−1.61	−1.79	−1.93
	$-NH_2$	−1.47	−1.63	−1.67	−2.01	−2.16	−2.37
	$-NHCH_3$	−1.54	−1.66	−1.77	−2.02	−2.23	−2.30
	$-N(CH_3)_2$	−1.55	−1.68	−1.80	−2.06	−2.25	−2.41

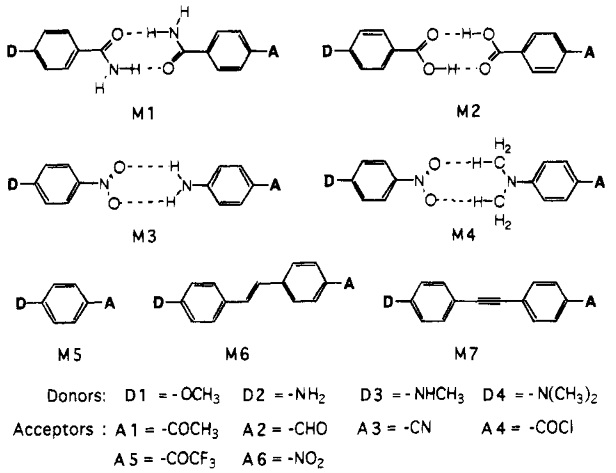

Figure 1. Structures and numbering scheme of motifs, donors, and acceptors.

observed in many crystal structures of ortho-substituted *p*-nitroanilines some of which adopt a noncentrosymmetric structure.[10] Recently, Desiraju reported a molecular recognition study wherein the nearly linear and relatively weaker C−H···O interactions have been optimized by the dimethylamino and nitro groups.[11] Hence, only such linear as well as planar conformations of dimers were considered here.

The AM1 approximation to MO theory has been successfully used in the studies of hydrogen bonds.[9] Geometrical optimizations were carried out using the program MOPAC.[12] The hyperpolarizabilities were calculated by the finite field method where the field was varied until the β and γ converge in the dipole moment and energy expansions.[13] The initial geometries of all monomers were obtained by the MMX calculations and those of the dimers were constructed from the monomers based on the averaged geometry of the dimers in crystals.[14,15] Only para-substituted compounds were considered here as they have higher hyperpolarizabilities compared to the other isomers.[16] To have a conformation similar to that in the crystal, the hydrogen bonding was constrained to be planar and the H···O distances along with the rest of the molecule were varied.[17] However, in a few cases, the terminal amino and dimethylamino groups tend to become slightly pyramidal. These groups were also constrained to be planar for two reasons: (1) their geometries are to be similar with all the other compounds and with those in the crystals; (2) very small energy differences (<0.1 kcal/mol) are observed between the pyramidal and planar conformations in either dimers or monomers.[18]

Results and Discussion

Hydrogen-Bonding Energies. The intermolecular bonding energies of the four motifs with different DA groups are given in Table 1. These energies have been calculated by subtracting the heat of formation of the two monomers from that of the dimer. Even though a large amount of this energy is due to hydrogen bonding in the dimer, the contributions of other types of interactions such as van der Walls and induced and permanent dipole−dipole interactions can also be significant. As there is no true energetic definition of the hydrogen bond, these intermolecular binding energies are collectively termed as the hydrogen-bonding energy (HBE).

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(17) In the absence of any constraint, some of the acid and amide dimers optimized to highly nonplanar, twisted, and nonacceptable conformations; however, both nitro dimers are well behaved. To make sure that a similar planar conformation is maintained in all four dimers, constraint in the dihedral angle was applied in all. While calculating the HBE, H_f values of molecules with similar constraints were considered.

(18) The maximum deviation of nitrogen from the plane of three connected atoms is only ~0.12 Å, whereas for complete pyramidality, according to sp^3 type bonding, is ~0.34 Å. Also, no significant deviation in β and γ are observed between the pyramidal and planar conformations.

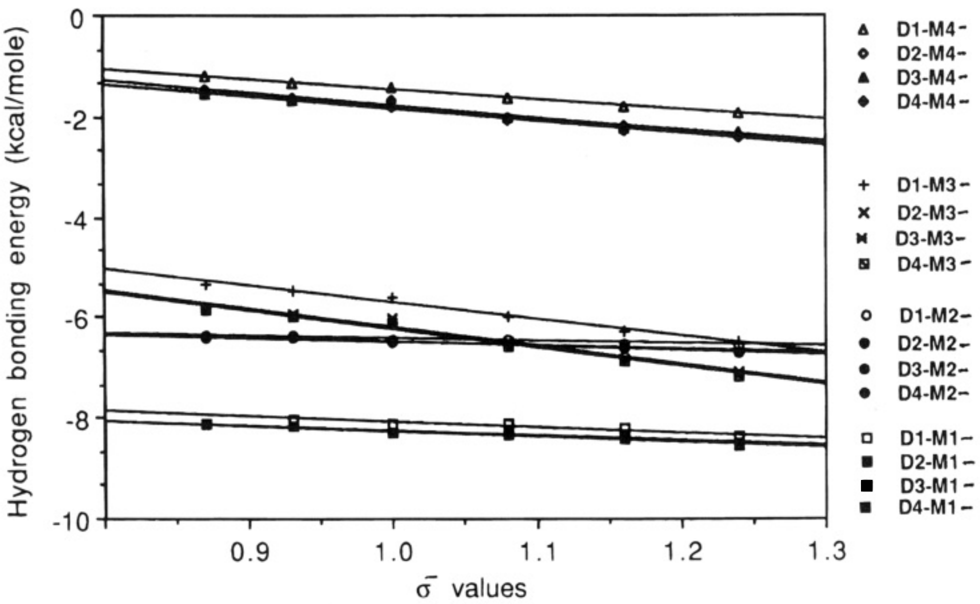

Figure 2. Variations in the intermolecular binding energies with the acceptor strength as indicated by their Hammett constants. Each motif contains four lines represented by four donors (D1 → D4). However, in the case of M1, M3, and M4, the lines corresponding to the three amino donors are merging with one another while in M2 all four are merged.

The HBE of dimethylamino dimers, containing C–H···O hydrogen bonds, are less stabilized compared to the other three dimers which involve stronger O–H···O or N–H···O interactions. Accordingly, in Figure 2, the lines of motif M4 are far above the others. When weaker acceptor groups are attached, HBE of M3 are less than those of M2, and when stronger groups are attached, these energies of M3 are larger than those of M2, resulting in the intersection of M2 and M3 HBE lines in Figure 2. Such a behavior could arise due to the following two reasons.[19]

(1) Underestimation of Acid and Amide Dimer Energies. Dannenberg observed that the acid and amide dimer HBE are underestimated when compared to the experimental HBE because of the intermolecular hydrogen–hydrogen repulsions.[9] Even though, M1 contains two N–H···O bonds compared to the two O–H···O bonds in M2, the HBE in the former are larger than those of the latter, indicating that the underestimation in the HBE of the N–H···O bond is less than that of the O–H···O bond. This underestimation in HBE, being constant for a given motif, might have moved up the whole set of M2 and to a lesser extent M1 values in Figure 2 and, therefore, should not affect the other results or conclusions.

(2) Additional Stability Gained in M3 and M4 Due to the Other Interactions. The induced polarization interactions between the two monomers may play a crucial role in M3 as well as in M4. Evidence that the binding between the two monomers in these motifs is due to not only hydrogen bonding but also to mutual polarization is provided by Figure 3 and Table 2, where the M3 and M4 motifs have large dipole moments compared to the combined dipole moments of the two monomers or other motifs. In motifs M1 and M2, such an increase is insignificant.

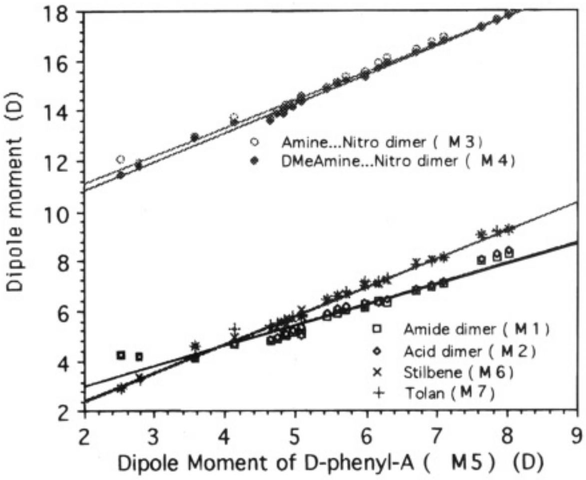

Figure 3. Dipole moment of all compounds containing other motifs with respect to those of motif M5. The dipole moment of compounds with M3 and M4 motifs are much higher than others.

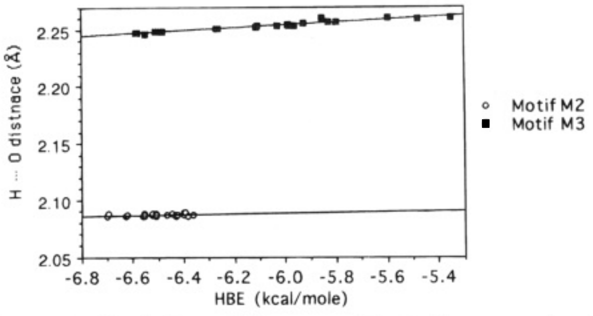

Figure 4. Variations of the mean H···O distances of each molecule with motifs M2 and M3 with respect to the hydrogen-bonding energies.

Effect of the DA Groups on HBE. In Figure 2, apart from M2, in the other three motifs, the HBE of the methoxy compounds ($D1{-}M_{\#}$) are smaller than other donors. However, there is not much variation among the amino donors. Given any donor, the HBE barely changes with the acceptor in M1 and M2 com-

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[19] The strength of the donors and acceptors are based on the Hammett constants, σ^{-} values and are from: Hansch, C., Leo, A.; *Substituent Constants for Correlation Analysis in Chemistry and Biology*; John Wiley & Sons: New York, 1979.

Table 2. Dipole Moments, μ (D), of Compounds Containing Motifs M1 to M7 and Substituted with Various Donor and Acceptor Groups

		moieties						
donor	acceptor	M1	M2	M3	M4	M5	M6	M7
$-OCH_3$	$-COCH_3$	4.3	4.3	12.1	11.5	2.5	3.0	3.0
	$-CHO$	4.2	4.2	12.0	11.8	2.8	3.3	3.3
	$-CN$	4.2	4.2	13.0	12.9	3.6	4.6	4.6
	$-COCl$	4.7	4.7	13.8	13.6	4.1	4.9	5.3
	$-COCF_3$	5.1	5.0	14.5	14.4	5.1	6.0	5.8
	$-NO_2$	6.3	6.3	15.4	15.4	6.0	7.1	7.0
$-NH_2$	$-COCH_3$	4.8	4.9	13.7	13.6	4.7	5.3	5.4
	$-CHO$	5.0	5.1	14.1	13.9	4.8	5.6	5.7
	$-CN$	5.8	5.9	14.9	14.8	5.4	6.5	6.5
	$-COCl$	6.1	6.2	15.6	15.5	6.0	7.0	7.2
	$-COCF_3$	6.8	6.9	16.5	16.4	6.7	7.9	7.8
	$-NO_2$	8.0	8.1	17.4	17.3	7.6	9.0	9.1
$-NHCH_3$	$-COCH_3$	4.9	5.0	14.0	13.9	4.8	5.4	5.5
	$-CHO$	5.2	5.3	14.3	14.1	5.0	5.7	5.8
	$-CN$	5.9	6.1	15.2	15.0	5.6	6.6	6.6
	$-COCl$	6.4	6.3	15.9	15.7	6.2	7.1	7.1
	$-COCF_3$	7.0	7.0	16.8	16.6	6.9	8.0	8.0
	$-NO_2$	8.1	8.2	17.7	17.6	7.9	9.2	9.2
$-N(CH_3)_2$	$-COCH_3$	5.0	5.1	14.2	14.1	4.9	5.5	5.6
	$-CHO$	5.2	5.3	14.6	14.4	5.1	5.8	5.9
	$-CN$	6.1	6.2	15.4	15.2	5.7	6.7	6.7
	$-COCl$	6.3	6.5	16.1	15.9	6.3	7.2	7.3
	$-COCF_3$	7.1	7.2	17.0	16.9	7.1	8.1	8.1
	$-NO_2$	8.2	8.4	17.9	17.8	8.0	9.3	9.3

pared to M3 and M4. As the acceptor strength increases, the HBE increases on average 0.27, 0.39, 0.81, and 1.25 kcal/mol in M2, M1, M4, and M3 dimers, respectively. Thus the effect of electron-donating and -withdrawing groups on hydrogen bonding is nearly negligible in acid and amide dimers and more significant in the two amino dimers as reflected by the closeness of the $D_\#$ lines and slopes of $M_\#$ lines in Figure 2.

Even though the HBE varies with respect to the DA strengths in some hydrogen-bonded motifs, there is almost negligible amount of intermolecular charge transfer in all the four motifs, suggesting a diminished charge flow through the hydrogen bond in the ground state.[20] However, the extra stability of M3 and M4 (greater slope in Figure 2) on varying the acceptor groups, can be due to enhanced mutual polarization interactions between the two monomers. Such an interaction could be ineffective in M1 and M2 because similar groups, viz, carboxylic acid or amide groups, face each other while forming the hydrogen bond. Very small variations in the HBE with the DA groups have also been observed by Dannenberg in the acid dimers.[8] The heteroacid dimers are favored to homodimers by ~1 kcal/mol, only when substituted with very strong DA groups. In general, when low-to-moderate DA groups are substituted, acids seldom form mixed dimers compared to those with stronger DA groups.[11]

Variation in the H···O Distance. As discussed earlier, the increase in the DA strength in motifs M3 and M4 increases the HBE, causing a variation in the H···O distance while such variation is minimum in M2 and M1 (Figure 4). The averaged H···O distances in M1 and M2 motifs are (2.045, 2.095 Å in M1 and 2.07, 2.105 in M2 for the two H···O distances, respectively) much longer than those found in the crystals (~1.8 Å). However, such a deviation is not observed in motifs M3 and M4 (in M3 and M4, the average H···O distances are 2.25 and 2.28 Å, respectively) where the H···O distances agree well with the X-ray distances (2.2−2.6 Å). In Figure 5, the variations in HBE in the four motifs with a pair of DA groups are shown with respect to the H···O distance. In M1 and M2, the H···O distance at the maximum HBE is greater than the X-ray distance, whereas in M3 and M4 these distances are in agreement with each other.

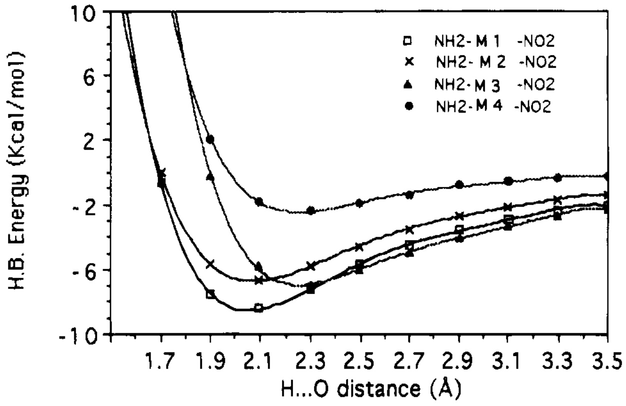

Figure 5. Variations in the HBE of $NH_2-M_\#-NO_2$ with the H···O distance.

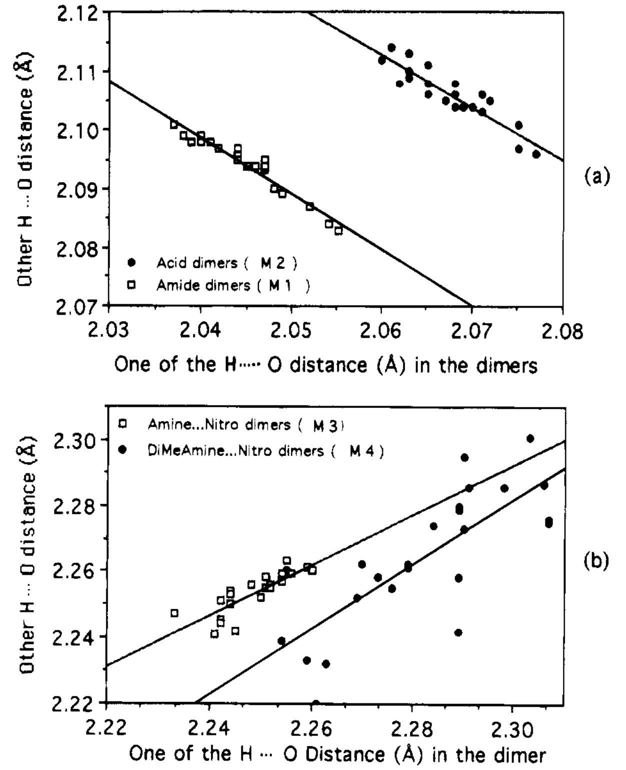

Figure 6. In the dimers, variation of one of the two H···O distances with the other is shown: (a) refers to the motifs M1 and M2 and (b) M3 and M4. The opposite slopes of the lines indicate that in M1 and M2 one decreases as other increases and in M3 and M4 both decrease or increase.

The relative variations of the two H···O distances in the four motifs are shown in Figures 6a,b. In motif M1, while one of the N−H···O distance decreases, the other increases (Figure 6a). In M2 also, a similar trend is observed with regards to O−H···O distances. Albeit there are some irregularities due to low C−H···O energies in M4, the H···O distances in M3 and M4 are not only symmetrical but also tend to decrease on increasing the DA strengths (Figure 6b). Even though

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[20] $NH_2-(M1\rightarrow M4)-NO_2$ (37, 25, 78, 40) ($\times 10^{-3}$); $(D1\rightarrow D4)-M3-NO_2$ (73, 78, 81, 81) ($\times 10^{-3}$); $NH_2-M3-(A1\rightarrow A4)$ (69, 72, 75, 76, 79, 78) ($\times 10^{-3}$) electrons.

Table 3. First-Order Hyperpolarizabilities, β ($\times 10^{-30}$ esu) of Compounds with Motifs M1 to M7 and Substituted with the Different DA Groups

		moieties						
donor	acceptor	M1	M2	M3	M4	M5	M6	M7
$-OCH_3$	$-COCH_3$	4	4	16	18	4	18	15
	$-CHO$	3	3	16	18	4	20	16
	$-CN$	4	4	14	15	3	18	15
	$-COCl$	5	5	19	21	5	27	21
	$-COCF_3$	7	7	21	24	6	31	27
	$-NO_2$	4	4	16	18	3	27	22
$-NH_2$	$-COCH_3$	7	7	20	22	6	29	25
	$-CHO$	7	8	20	22	6	31	26
	$-CN$	7	7	19	20	5	31	26
	$-COCl$	9	9	24	25	8	42	35
	$-COCF_3$	10	10	25	28	9	49	41
	$-NO_2$	7	8	20	22	6	44	35
$-NHCH_3$	$-COCH_3$	8	9	23	24	7	33	28
	$-CHO$	9	10	23	24	8	35	30
	$-CN$	9	10	22	22	7	36	30
	$-COCl$	11	11	27	28	10	47	39
	$-COCF_3$	12	12	29	31	12	55	46
	$-NO_2$	9	10	24	25	8	49	40
$-N(CH_3)_2$	$-COCH_3$	10	11	26	27	9	36	31
	$-CHO$	11	11	26	27	9	39	33
	$-CN$	10	11	24	25	8	39	33
	$-COCl$	12	13	30	31	12	51	43
	$-COCF_3$	13	14	32	34	14	60	50
	$-NO_2$	11	12	26	27	9	54	44

both M1 and M3 motifs contain N–H···O bonds, the optimized H···O distances in the former are much shorter than the latter. These results indicate that in the acid and amide dimers, apart from the H···H repulsions, the O···O or O···N repulsions play a crucial role in the underestimation of the HBE and cause the overestimation of the H···O distances. Thus, the difference between the carboxyl dimers and amino dimers can be attributed to the conglomeration of many forces such as stronger hydrogen bonds, repulsive forces, and the mutual polarization interactions between the two hydrogen-bonded molecules.

Hyperpolarizabilities in Some HB Motifs. Phenyl, stilbene, and tolans substituted with similar DA groups were also studied to compare the hyperpolarizabilities with those of the hydrogen-bonded motifs. The β and γ values of all these compounds are given in Tables 3 and 4, respectively. In any set of DA groups, the β is least for M5, increases marginally in M1 and M2 and further in M3 and M4. In M7 and M6, the β value further increases, with M6 having the maximum value. Although the γ values also show a similar trend, the difference between M4 and M7 is rather large.

It is generally understood that the β value is enhanced when there is a low-lying ground-to-excited-state transition with a large change in the dipole moment and a large transition dipole moment. In contrast, the γ value is generally enhanced with larger conjugation and the effect of DA groups also being moderately significant. From Tables 3 and 4, it is obvious that for any given set of DA groups, the β and γ of hydrogen-bonded motifs are small compared to the stilbene and tolan systems. If there were to be a charge transfer through the hydrogen bond from donor to acceptor molecule in the excited state, then one would expect similar values of β and γ as those of stilbenes and tolans where the charge transfer takes place through π-conjugation. This suggests that even in the excited state there is not much significant charge transfer from donor to acceptor through hydrogen bonding.

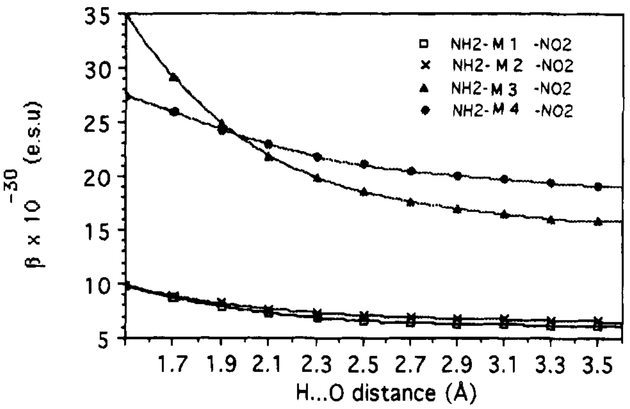

Figure 7. Variation in the β with the H···O distance in the $NH_2-M_\#-NO_2$ dimers.

Table 4. Second-Order Hyperpolarizabilities, γ ($\times 10^{-36}$ esu), of Compounds with Motifs M1 to M7 and Substituted by the Different DA Groups

		moieties						
donor	acceptor	M1	M2	M3	M4	M5	M6	M7
$-OCH_3$	$-COCH_3$	20	20	28	36	8	127	101
	$-CHO$	20	20	27	34	7	126	100
	$-CN$	20	19	24	29	6	125	100
	$-COCl$	21	21	31	39	9	147	117
	$-COCF_3$	23	22	33	44	11	166	131
	$-NO_2$	20	19	28	35	7	146	115
$-NH_2$	$-COCH_3$	22	22	31	39	9	156	125
	$-CHO$	21	21	30	36	8	154	125
	$-CN$	21	21	27	33	6	154	122
	$-COCl$	23	23	34	42	10	191	148
	$-COCF_3$	24	24	37	46	12	217	171
	$-NO_2$	21	21	32	38	8	192	151
$-NHCH_3$	$-COCH_3$	26	27	38	45	13	180	143
	$-CHO$	26	26	37	43	12	180	143
	$-CN$	26	27	34	38	9	181	142
	$-COCl$	27	28	42	49	15	219	172
	$-COCF_3$	29	29	44	53	17	249	196
	$-NO_2$	26	26	39	44	12	221	174
$-N(CH_3)_2$	$-COCH_3$	30	31	44	50	16	198	159
	$-CHO$	29	30	43	48	15	198	159
	$-CN$	29	31	40	44	12	199	158
	$-COCl$	31	32	48	54	19	241	192
	$-COCF_3$	33	34	51	59	22	277	219
	$-NO_2$	30	30	45	50	16	248	194

Effect of the DA Groups on the β and γ. Even though there is not much difference in the HBE values between the three amino donors, the β and γ values increase gradually from D1 → D4. However, in the acceptors A1 → A6, the variations in the β and γ values (Tables 3 and 4) are not uniform. Within the same motif and donor, compounds containing cyano or nitro groups tend to have lower β and γ values than the other acceptors. The other four acceptors, being derived from the carbonyl group, may have highly polarizable excited states by which the β and γ values can be enhanced compared to the cyano and nitro groups. An analogous observation has been made by Matsuzawa and Dixon in some cyano and nitro compounds where β_{calc} is lower than the β_{exp} values.[21]

In Figure 7, the variations in the β of four HB motifs containing amino and nitro groups are shown with respect to the H···O distance. At longer distances, the β is essentially the sum of the two monomer values, but as the monomers approach each other, the electrostatic interactions play a role and β is the sum of those of the

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(21) Matsuzawa, N.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6232.

two polarized monomers. The extent of polarization being smaller in the M1 and M2 dimers, β and γ change very little compared to the motifs M3 and M4 where the mutual polarization enhances the charge transition within the individual molecules, which in turn can lead to a larger transition dipole moment. At shorter distances, the β values of M4 are smaller than those of M3. This could be due to less induced polarization of M4 as the methyl groups can cause the screening effect for the mutual polarization.

The effect of β value on polarization was studied in the two dimers involving at least one symmetric monomer. The β of the dimer of dinitrobenzene and *p*-nitroaniline ($NO_2-M5-NO_2 \cdots NH_2-M5-NO_2$) is 10×10^{-30} esu compared to 6×10^{-30} esu for *p*-nitroaniline. Similarly, the β value of the dimer dinitrobenzene and phenylenediamine ($NO_2-M5-NO_2 \cdots NH_2-M5-NH_2$) is 1.6×10^{-30} esu as compared to the zero values for the individual monomers. Had there been any charge transfer between the two hydrogen-bonded molecules in these cases, the enhancement in β would have been much larger. The small β value in the second dimer arises purely due to mutual polarization.

Conclusions

AM1 calculations on some of the DA-substituted hydrogen-bonded dimers indicate that the hydrogen-bonding energies do not vary much in acid and amide dimers with DA groups, unlike the nitro$\cdots$amino dimers. In addition, these studies reveal that the stronger hydrogen bonding may not be conducive to any charge transfer vis-á-vis the hyperpolarizabilities in acid and amide dimers. Although there is no significant charge transfer in the two nitro$\cdots$amino dimers, mutual polarization enhances the β value to some extent. However, in stilbenes and tolans π-conjugation contributes to the further rise in these values. Thus, the β values of these nitro$\cdots$amino dimers are better than those of the acid and amide dimers and as these groups are proved to be efficient steering groups for noncentrosymmetric patterns, there a good chance of generating effective SHG crystals. On the basis of these studies, it is suggested that the hydrogen bonding between groups that are conducive in creating large mutual polarization and generating noncentrosymmetric crystal structures can be utilized in developing better SHG materials at supramolecular level.

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