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A Molecular Orbital Study on the Hole Transport Property of Organic Amine Compounds

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Reorganization energy (λ_1) in the ionization process of organic amines and that (λ_2) of the electron attaching process of amine cation radicals are evaluated with AM1, ab initio MO, and DFT methods, where dimethylaniline, methyldiphenylamine, and triphenylamine are adopted as a model of a hole transport material. The total λ value ($=\lambda_1 + \lambda_2$) decreases in the order dimethylaniline > methyldiphenylamine > triphenylamine, which agrees well with an increasing order of experimentally reported hole transport mobility of diamines that are dimers of above-mentioned amines, *N*,*N*′-tetraphenyl-[1,1′-biphenyl]-4,4′-diamine < *N*,*N*′-dimethyl-N,N′-diphenyl-[1,1′-biphenyl]-diamine < *N*,*N*′-tetramethyl-[1,1′-biphenyl]-4,4′-diamine. This relation is reasonably explained with Marcus theory, since the λ value is directly related to the activation energy of hole transfer from one amine cation radical to a neighboring neutral amine, according to Marcus theory. The geometry changes in the ionization process are inspected to find a determining factor for λ. The large λ value of dimethylaniline arises from the fact that the pyramidal structure of dimethylaniline changes to the planar structure upon the ionization. On the other hand, the small λ value of triphenylamine might be attributed to the fact that the bond angle about the N atom changes little upon the ionization because both neutral triphenylamine and its cation radical are planar about the N atom. From these results, we might provide a prediction that a planar amine is a good candidate for a hole transport material.

Introduction

Triphenylamine derivatives are widely used as a hole transport material in an organic electroluminescent device (OEL), which is expected as a new excellent emitting material.[1−3] Much effort has been made to find a relation between the hole transport property and molecular structures of triphenylamine derivatives, in an attempt to present a guideline for device design,[2c,4−7] since such a relation is more useful for finding a new excellent hole transport material and improving the hole transport mobility. For instance, Saito and co-workers reported an interesting and useful relation between the stability of the thin film and molecular structure of amine.[2c] Also, Aratani and co-workers investigated the hole transport property of molecularly doped polymer (MDP) systems, in which triphenylamine derivatives were used as a dopant of polycarbonates, and found that the hole transport ability became better with an increase of the HOMO electron density of the triphenylamine moiety.[7] However, its reason is still ambiguous.

Recently, Pacansky and co-workers theoretically investigated triphenylamine with the ab initio MO method and estimated the activation barrier as the energy difference between geometries of neutral and ionized triphenylamine.[8] Although they estimated the barrier for hole transport according to Holstein,[9] the barrier might be easily estimated on the basis of Marcus theory,[10] too: The hole transport is the reverse of electron transfer, and the electron transfer rate constant is determined by a free energy difference (ΔG°), an electron coupling matrix element (H_{AB}) between electron donor and acceptor, and a reorganization energy (λ) through Marcus theory (eq 1):

$$k_{et} = (4\pi^2/h)H_{AB}{}^2(4\pi\lambda RT)^{-1/2}\exp\{-(\Delta G^\circ + \lambda)^2/(4\lambda RT)\} \tag{1}$$

Since a hole transfers from one amine cation radical to the neighboring neutral amine molecule in the hole transfer materials (eq 2), ΔG° is zero in this hole transfer (note that the right- and left-hand sides of eq 2 are the same), and therefore, the activation barrier $\Delta G^\ddagger$ should be the same as the reorganization energy $\lambda/4$. As a result, k_{et} is represented with eq 3.

$$NR_3(A) + {}^{\bullet}NR_3{}^+(B) \rightarrow NR_3{}^+(A) + NR_3(B) \tag{2}$$

$$k_{et} = (4\pi^2/h)H_{AB}{}^2(4\pi\lambda RT)^{-1/2}\exp\{-\lambda/(4RT)\} \tag{3}$$

Although eq 3 gives rise to a too strong dependence of k_{et} on λ, the semiquantitatively correct relation between k_{et} and λ would be obtained with this eq 3.[11] The reorganization energy λ can be estimated as a sum of differences between vertical and adiabatic ionization potentials of neutral amine and between vertical and adiabatic electron affinities of the amine cation radical, as shown in Scheme 1. Thus, one might expect that the hole transport mobility would be mainly determined by the reorganization energy λ.

If the above expectation is correct, we might present a useful guideline for molecular design of a good hole transport material; in other words, the small reorganization energy in the electron transfer reaction is one of the important conditions for a good hole transport material. However, little work has been performed to ascertain whether the hole transport mobility is related to the reorganization energy, to our best knowledge.[12]

In this theoretical work, we investigated the ionization potential of several organic amines and the electron affinity of

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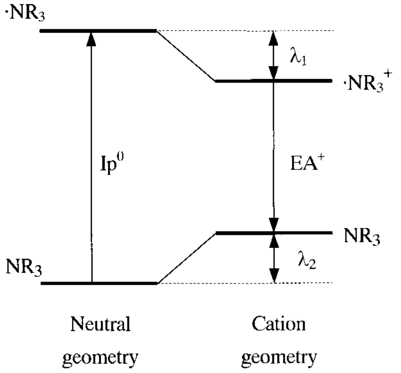
SCHEME 1



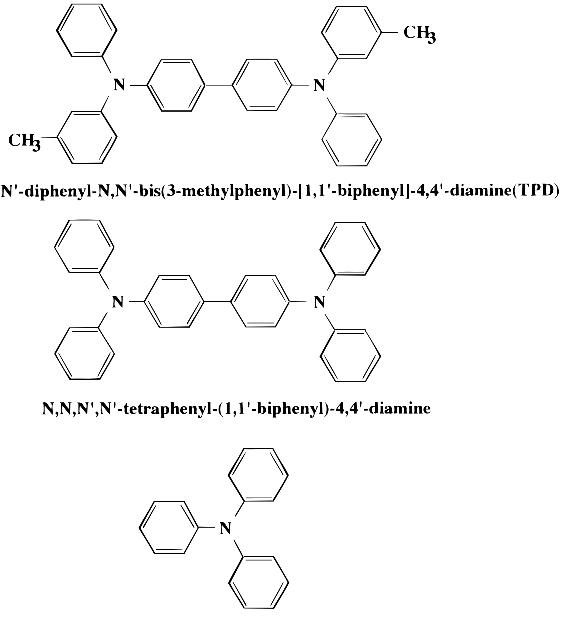
Ip^0 : Vertical ionizaiton potential of neutral molecule

EA^+: Vertical electron affinity of cation radical

λ_1: Reorganization energy of cation radical

λ_2: Reorganizaiton energy of neutral molecule

CHART 1



N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine(TPD)

N,N,N',N'-tetraphenyl-(1,1'-biphenyl)-4,4'-diamine

Triphenylamine

their cation radicals with semiempirical AM1,[13] ab initio MO, and DFT methods. Our purposes here are to estimate the reorganization energy in hole transfer, to examine whether a relation between the reorganization energy and the hole transport ability exists, and to present a relation between the reorganization energy and the amine molecular properties.

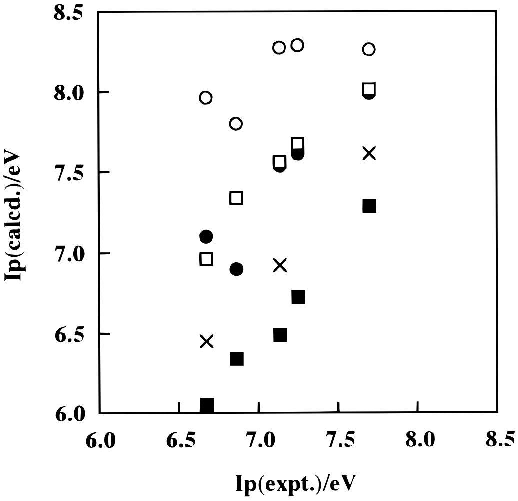


Figure 1. Theoretically estimated ionization potentials[a] vs experimental ionization potentials[b]. [a]ΔSCF calculations with AM1, ab initio MO (HF/6-31G[*]//HF/3-21G[*]), DFT/3-21G[*] methods. [b]Triphenylamine, benzidine, dimethylaniline, diphenylamine, and aniline in the increasing order of experimental ionization potentials. Key: (○) AM1(Koopmans); (●) HF/6-31G[*]//HF/3-21G[*](Koopmans); (□) AM1/ROHF(ΔSCF); (■) HF/6-31G[*]//HF/3-21G[*](ΔSCF); (×) DFT/3-21G[*].

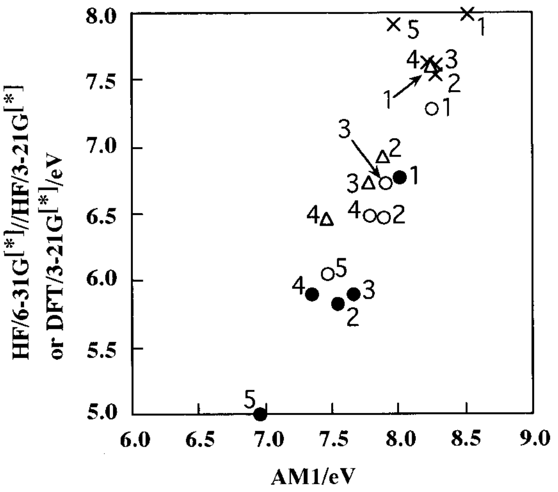
Computations. *N*,*N*′-Diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD; see Chart 1) is one of the representative hole transport materials,[2a] and the hole transport mobility was reported experimentally in *N*,*N*′-tetraphenyl-[1,1′-biphenyl]-4,4′-diamine, *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-[1,1′-biphenyl]-diamine, and *N*,*N*′-tetramethyl-[1,1′-biphenyl]-4,4′-diamine.[5a] Since their sizes are considerably large, we investigated here the half-molecule (see Chart 1) such as triphenylamine, methyldiphenylamine, and *N*,*N*′-dimethylaniline,[14] since the properties of these hole transport materials are reasonably expected to reflect in the half-molecule. Actually, Pacansky et al. investigated triphenylamine as a model of a hole transport material.[8] Because triphenylamine and methyldiphenylamine are still large for ab initio MO calculations including electron correlation effects, we adopted here semiempirical AM1 MO,[13] ab initio MO at the Hartree−Fock level, and DFT methods.

In ab initio MO calculations, geometries were optimized with the usual 3-21G basis set.[15] A d-polarization function was added only on the N atom,[16] since we expected that the bond angle about the N atom would be changed upon ionization and therefore the bond angle about the N atom should be correctly calculated to estimate the reorganization energy. This type of basis set is represented by a superscript [*] here. The ionization potential was evaluated with 3-21G[*] and 6-31G[*] basis sets.[17] The one-electron oxidized state (or cation radical) of the amine was optimized with both restricted open-shell Hartree−Fock (ROHF) and unrestricted open-shell Hartree−Fock (UHF) methods.

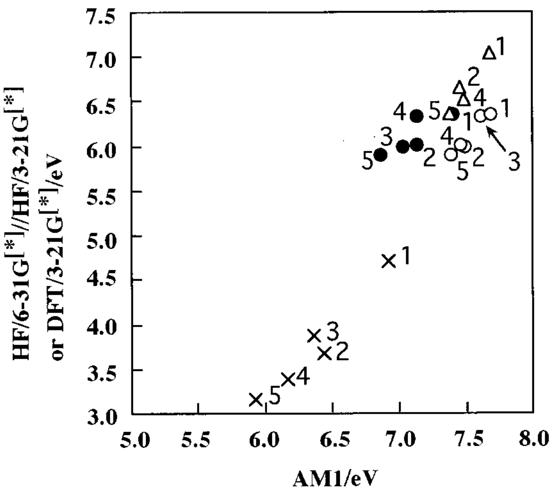
In DFT calculations, we adopted the usual B3LYP functional that involves the gradient correction of the exchange functional by Beck[18] and the correlational functional by Lee, Yang, and Parr.[19] The 3-21G[*] basis set was also used in DFT calculations such as that in ab initio MO calculations.[20] All these calculations were carried out with the Gaussian 94 program.[21]

Results and Discussion

Ionization Potentials (I_p) of Neutral Amines and Electron Affinities (EA) of Amine Cation Radicals. Since one of our purposes here is to evaluate correctly the reorganization energy in the ionization process of the neutral amine and the electron attaching process of the amine cation radical, the computational method employed must give reliable results on geometries and ionization potentials of these compounds, at least. In AM1, ab initio MO, and DFT calculations, the optimized N−C distance of triphenylamine (1.413, 1.417, and 1.423 Å, respectively) agrees well with the experimentally reported value (1.419 Å).[22] In Figure 1, theoretically calculated ionization potentials are compared with the corresponding experimental values.[23,24] Apparently, Koopmans theory with the AM1 and ab initio MO (HF/6-31G[*]//HF/3-21G[*]) methods gives incorrect results even in a qualitative sense. On the other hand, ΔSCF calculations with the AM1 and ab initio MO methods yield semiquantita-



a)Ionization potentials of neutral amines



b)Electron affinities of amine cation radicals

Figure 2. Ionization potentials of neutral amines and electron affinities of amine cation radicals. Comparison of the AM1 method with DFT/3-21G$^{[*]}$ and ab initio MO (HF/6-31G$^{[*]}$//HF/3-21G$^{[*]}$) methods. (i) Relations with the ab initio MO method: (○) ΔSCF(ROHF) calculation; (●) ΔSCF(UHF) calculation; (×) Koopmans theory. (ii) Relation with DFT method: (△) ΔSCF(ROHF) calculation. Key: (1) aniline; (2) *N,N*-dimethylaniline; (3) diphenylamine; (4) methyldiphenylamine; (5) triphenylamine.

tively correct results. The best agreement is observed in the DFT calculations, as expected, where the error is less than about 0.2 eV.

Interestingly, the I_p value calculated with the AM1 method linearly increases with the value calculated with the ab initio MO method, when the ΔSCF calculation is employed, as shown in Figure 2a. Again, Koopmans theory gives rise to a poor relation between AM1 and ab initio MO values. The ΔSCF (AM1) calculations also give a moderately good linear relation with the DFT values. In those relations, the ΔSCF(ROHF) calculations yield better agreement than the ΔSCF(UHF) calculations. This is probably because the spin contamination considerably occurs in the UHF calculation of the amine cation radical; for instance, $\mathbf{S}^2 = \sim 1.35$ was calculated with UHF/6-31G$^{[*]}$ in dimethylaniline.

Electron affinity of the amine cation radical should be reliably estimated, too. Since the electron affinities (EA) of amine cation radicals have not been experimentally reported, we cannot examine the reliability of AM1, ab initio MO, and DFT methods by comparing the calculated EA value with the experimental one. Here, we compared the calculated EA values between AM1 and DFT methods. As shown in Figure 2b, an almost linear relation is observed between AM1 and DFT methods, when the ROHF method was adopted in AM1 calculations. However, a poor relation exists between AM1 and DFT methods, when the UHF method was adopted in the AM1 calculation. The AM1 calculated values are also compared with the ab initio MO (HF/6-31G$^{[*]}$//HF/3-21G$^{[*]}$) calculated ones. As shown in Figure 2b, an approximately linear relation is observed between AM1 and ab initio MO calculated values, when the ROHF method is adopted.

These results suggest that the DFT method is the best, as expected, while the AM1 MO method, as well as the ab initio MO method, seems reliable in a semiquantitative sense at least, and that the ROHF method is much better than the UHF method for investigation of these amine cation radicals; in other words, the UHF method should not be used.

Reorganization Energy (λ) in the Ionization Process of the Neutral Amine and the Electron Attaching Process of the Amine Cation Radical. The reorganization energy λ_1 in the ionization process can be estimated as a difference between the vertical ionization potential and adiabatic ionization potential; i.e., λ_1 is a stabilization energy by geometry relaxation of the amine cation radical (see Scheme 1). The reorganization energy λ_2 in the electron attaching process is an energy difference between the vertical electron affinity and adiabatic electron affinity of the amine cation radical. The total reorganization energy λ in the electron transfer reaction (and the hole transfer reaction) is a sum of λ_1 and λ_2; $\lambda = \lambda_1 + \lambda_2$.

To estimate λ_1, we need to optimize the cation radical of the amine derivative. We adopted the ROHF method in the optimization, since the UHF calculation causes a considerable spin contamination (vide supra). Since the λ_1 value has not been experimentally reported, we cannot compare calculated values with the experimental ones. Here, we compare again the calculated λ_1 values of AM1 and ab initio MO (HF/6-31G$^{[*]}$//HF/3-21G$^{[*]}$) methods with those of the DFT method. The λ_1 values from AM1 calculation roughly agree with those from DFT calculation, as shown in Figure 3a. However, the λ_1 values from ab initio MO calculation are much larger than those from DFT calculation except for λ_1 of triphenylamine. Moreover, the λ_1 value from ab initio MO calculation decreases in the order aniline > methyldiphenylamine > dimethylaniline > triphenylamine, which does not agree with the decreasing order provided by AM1 and DFT calculations. From these results, it might be reasonably suggested that the AM1 method, as well as the DFT method, would be useful for estimating the λ_1 value in the ionization process, while the ab initio MO method seems less useful than the AM1 method. As shown in Figure 3b, the λ_2 values from the AM1 calculation approximately agree with those from the DFT calculation, while the λ_2 values from the ab initio MO calculation are much larger than those from the DFT calculation.

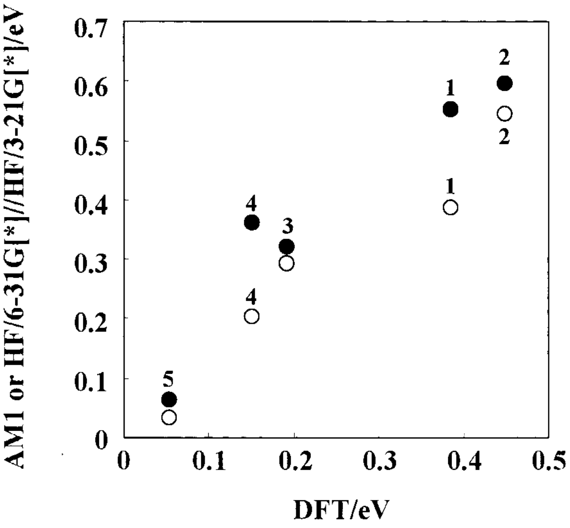
The above results provide the following conclusions; the DFT method is considered the best for the evaluation of λ, and the AM1 method might be also applied for qualitative estimation of λ value, while the ab initio MO method is considered less useful than the AM1 and DFT methods. This is probably because electron correlation effects must be taken into consideration in the λ estimation.

λ Value and the Hole Mobility. In Table 1, we compare the experimentally estimated hole transfer mobility[5a] with the λ value. Apparently, the λ(AM1) and λ(DFT) values decrease

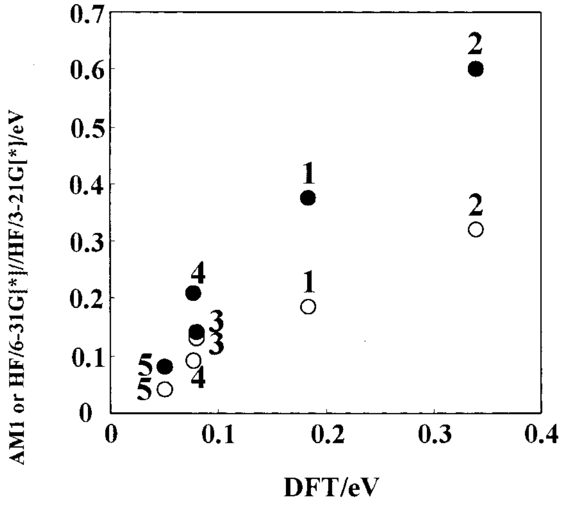
TABLE 1: Reorganization Energies and Hole Mobilities of Aniline (1), Benzidine (2), *N*,*N*-Dimethylaniline (3), Methyldiphenylamine (4), and Triphenylamine (5)

	1			2			3			4			5		
reorganization energy/eV	λ	λ_1	λ_2	λ	λ_1	λ_2	λ	λ_1	λ_2	λ	λ_1	λ_2	λ	λ_1	λ_2
AM1(ROHF)	0.572	0.386	0.186	0.868	0.546	0.322	0.424	0.293	0.131	0.295	0.203	0.092	0.075	0.033	0.042
HF/6-31G[*]//HF/3-21G[*]	0.929	0.552	0.377	1.195	0.595	0.600	0.462	0.320	0.141	0.569	0.361	0.208	0.147	0.064	0.082
DFT(B3LYP)/3-21G[*]	0.569	0.385	0.184	0.789	0.449	0.340	0.272	0.192	0.080	0.227	0.150	0.077	0.103	0.053	0.050
k_{rel}(AM1/ROHF)[a]								1.4×10^{-2}			6.0×10^{-2}			1.00	
k_{rel}(DFT)[a]								1.2×10^{-1}			2.0×10^{-1}			1.00	
hole mobility[b]								not obsd			2.0×10^{-8}			2.7×10^{-6}	

[a] The relative value was estimated from Marcus theory, according to eq 3, under the assumption that the electronic coupling matrix element is similar in these amine compounds. [b] Reference 5a.



a) Ionization process neutral amines



b) Electron attaching process of amine cation radical

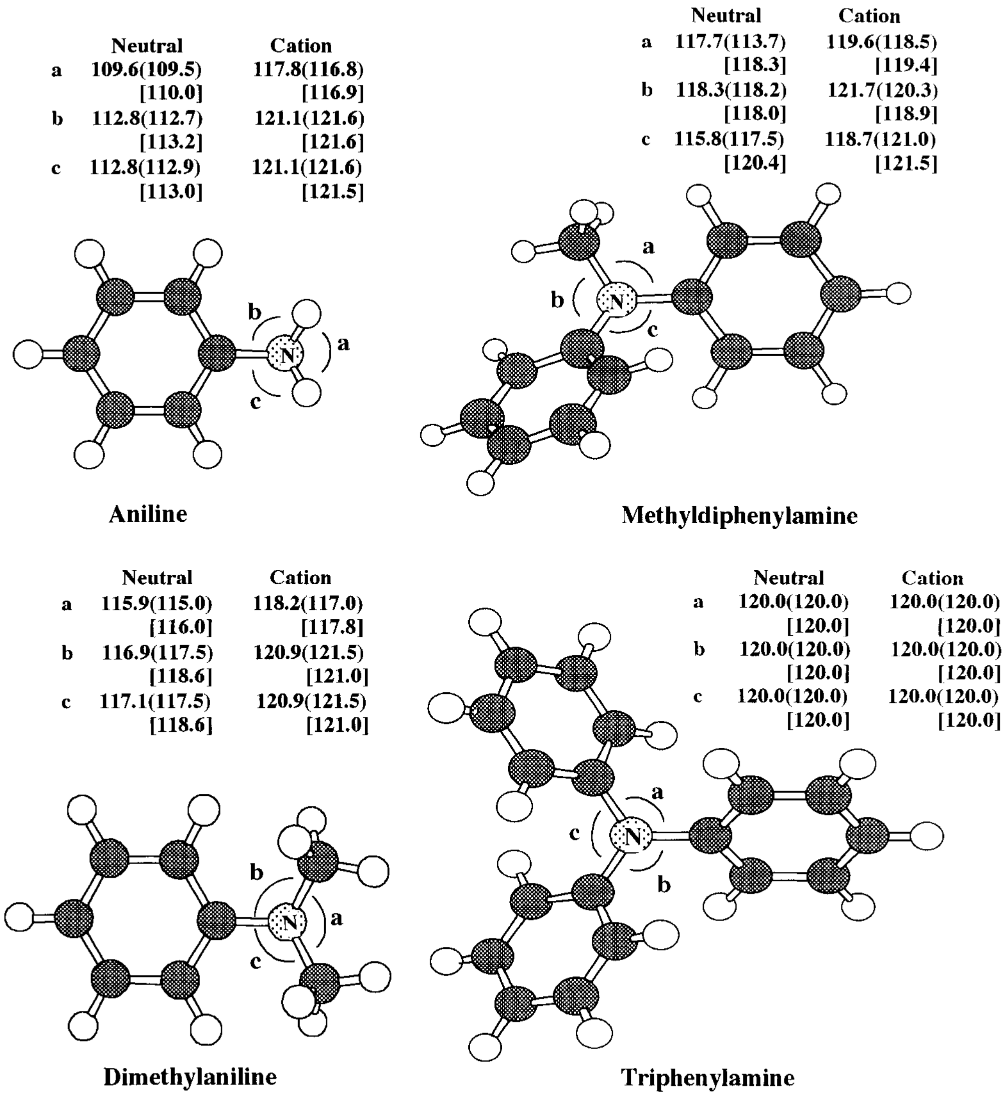
Figure 3. Reorganization energy (λ) calculated with AM1, ab initio MO (HF/6-31G[*]//HF/3-21G[*]), and DFT/3-21G[*] methods. (a) All the values were calculated with the ΔSCF(ROHF) method. Key: (○) AM1; (●) ab initio MO; (1) aniline; (2) *N*,*N*-dimethylaniline; (3) diphenylamine; (4) methyldiphenylamine; (5) triphenylamine.

in the order dimethylaniline > methyldiphenylamine > triphenylamine. It should be noted that this decreasing order agrees well with the increasing order of hole mobility, *N*,*N*′-tetramethyl-[1,1′-biphenyl]-4,4′-diamine < *N*,*N*′-dimethyl-N,N′-diphenyl-[1,1′-biphenyl]-4,4′-diamine < *N*,*N*′-tetraphenyl-[1,1′-biphenyl]-diamine. This can be easily understood on the basis of Marcus theory, since the activation barrier ($\Delta G^{\ddagger}$) for the electron (hole) transfer is taken to be the same as $\lambda/4$, as discussed above (see eq 3). We can estimate the relative value of the rate constant for the electron (hole) transfer reaction with Marcus theory, using the above-estimated λ value, under the assumption that the electronic coupling matrix element (H_{AB}) is not different very much in these amine derivatives. This assumption seems reasonable, since similar amine derivatives are compared to each others. Interestingly, the relative values of rate constant for hole transfer agree well with the relative values of experimentally estimated hole mobility, as shown in Table 1, when the λ(AM1) values were adopted. The relative rate constants calculated from λ(DFT) increase in the order dimethylaniline < methyldiphenylamine < triphenylamine, to a lesser extent than the experimental values. This result indicates that although we need to take into consideration H_{AB} for the quantitatively correct value of hole transport mobility, the reorganization energy is one of the important factors to determine the hole transport mobility. The λ values from ab initio MO calculation decrease in the order methyldiphenylamine > dimethylaniline > triphenylamine, which does not agree with the experimental result even in a qualitative sense.

The above result clearly shows that the reorganization energy (λ) is considered a good measure for hole mobility and that DFT and AM1 methods seem reliable for investigation of hole transport mobility.

Geometry Changes in Ionization Process. The next issue to be investigated is to find a determining factor for the reorganization energy. To find it, we inspected the geometry change by the ionization of the neutral amine (note that the reverse geometry change occurs in the electron attaching process of the amine cation radical). In dimethylaniline, the pyramidal structure about the N atom changes to the planar one upon ionization, as shown in Figure 4. A similar geometry change is observed in methyldiphenylamine, as follows; this molecule is pyramidal about the N atom, while the deviation from the planar structure is less than that in dimethylaniline. Upon the ionization, this molecule becomes completely planar about the N atom, too. On the other hand, triphenylamine is planar even in the neutral species, and of course, its cation radical is planar.

These geometry changes observed in dimethylaniline and methyldiphenylamine are deeply related to the λ value. We adopted here the sum of bond angles (θ) about the N atom to represent the extent of deviation from the planar structure in neutral amine. If θ is 360°, the molecule is planar about the N atom. The pyramidal structure becomes more sharp as θ decreases from 360°. Apparently, the λ value decreases as the θ value approaches 360°, as shown in Figure 5. From these results, the following conclusions are extracted: (1) a cation radical of an organic amine is planar about the N atom, (2) if an amine is pyramidal about the N atom in the neutral state, the ionization must induce a geometry change about the N atom



Aniline

	Neutral	Cation
a	109.6(109.5) [110.0]	117.8(116.8) [116.9]
b	112.8(112.7) [113.2]	121.1(121.6) [121.6]
c	112.8(112.9) [113.0]	121.1(121.6) [121.5]

Methyldiphenylamine

	Neutral	Cation
a	117.7(113.7) [118.3]	119.6(118.5) [119.4]
b	118.3(118.2) [118.0]	121.7(120.3) [118.9]
c	115.8(117.5) [120.4]	118.7(121.0) [121.5]

Dimethylaniline

	Neutral	Cation
a	115.9(115.0) [116.0]	118.2(117.0) [117.8]
b	116.9(117.5) [118.6]	120.9(121.5) [121.0]
c	117.1(117.5) [118.6]	120.9(121.5) [121.0]

Triphenylamine

	Neutral	Cation
a	120.0(120.0) [120.0]	120.0(120.0) [120.0]
b	120.0(120.0) [120.0]	120.0(120.0) [120.0]
c	120.0(120.0) [120.0]	120.0(120.0) [120.0]

Figure 4. Changes of bond angles (degree) about the N atom upon ionization of amines: out of parentheses, AM1; in parentheses, HF/3-21G[*]; in brackets, DFT/3-21G[*].

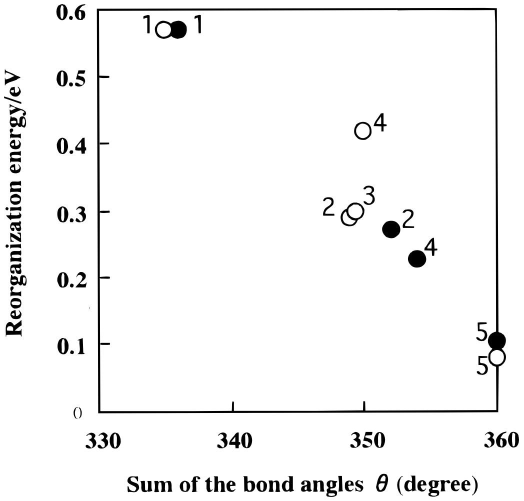


Figure 5. Relation between the reorganization energy λ and the sum of the angles about the N atom: (○) AM1; (●) DFT; (1) aniline; (2) diphenylmethylamine; (3) methyldiphenylamine; (4) dimethylaniline; (5) triphenylamine.

from a pyramidal structure to a planar one, (3) the λ value is small in triphenylamine because it is planar in the neutral species and does not need to change into the planar structure upon the ionization, and (4) the λ value is large in dimethylaniline because it is pyramidal in the neutral species and must cause the geometry change to the planar structure upon the ionization.

Conclusions

The ionization potential of neutral organic amines and the electron affinity of those cation radicals were investigated with AM1, ab initio MO, and DFT methods. As expected, the DFT method provides the most reliable results, while the AM1 method seems useful in a semiquantitative sense. However, the ab initio MO method gives rise to poor results of the reorganization energy. Thus, the ab initio MO method seems less useful for investigating the hole transfer mobility of organic amines.

The activation barrier for hole transport depends on the reorganization energies in the ionization process of the neutral amine and the electron attaching process of the amine cation radical, according to Marcus theory. Actually, the hole transport mobility increases as the theoretically evaluated λ value decreases. The important geometry change in the ionization process is that the pyramidal structure about the N atom becomes planar upon the ionization. This is because the amine cation radical tends to take a planar structure about the N atom. The reorganization energy would be mainly related to this geometry change. When an amine is planar in the neutral species, the reorganization energy would be small, since the geometry does not need to change very much upon the ionization. Certainly, the λ value decreases as the geometry about the N atom becomes planar in the neutral amines. From these results, we propose here several guidelines for design of hole transport material: (1) a good hole transport material must have a small reorganization energy in the ionization process, (2) a planar amine is expected to be a good material for hole transport; since the amine cation radical is planar about the N atom, the reorganization energy upon the ionization would become small in such a planar amine, and (3) the geometry fixation that suppresses the geometry change in the ionization process would be recommended to decrease the reorganization energy; one example is 4-(3,6-di-*tert*-butylcarbazol-9-yl)benzonitrile in which the ethylene bridge is introduced between two phenyl groups of triphenylamine (see ref 25). This compound and its analogue have been recently used as a fluorescent material,[25] and at the same time, they are also expected to exhibit a small reorganization energy in hole transfer.

Of course, we need to investigate the H_{AB} term to present a more quantitatively correct estimation of hole transport mobility. However, the above-mentioned results clearly show that the reorganization energy is one of the important factors for hole transport and that the geometry change about the N atom is a key factor for the reorganization energy.

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