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Ab Initio Computational Studies on the Structures and Energetics of Hole Transport Molecules: Triphenylamine

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Triphenylamine neutral and hole (radical cation) molecules are optimized by ab initio Hartree–Fock calculations at the 3-21G basis set. Modest changes in geometry are computed upon oxidation. The unpaired electron is 59% localized on the amine nitrogen atom. The energy barrier for the hopping process involving the electron transfer between a neutral and ionized (hole) triphenylamine is 0.15 eV. The vibrational mode that is primarily associated with the change in geometry upon hole formation is the C–N stretching mode.

There is a class of organic amorphous material, molecularly doped polymers (MDP), which is widely used in copier and laser printer applications.[1] The drift mobility of these materials is rather small, of the order of 10^{-6}—10^{-7} $cm^2\ V^{-1}\ s^{-1}$ near optimum doping, many orders smaller than values found in semiconductors involving extended band states. The particular hopping conduction process involved in this type of material became apparent through investigations using transient drift mobility techniques.[2,3] A comparison of recent charge transport models has been given by Schein.[4] From these measurements it has been established that the mobility is highly field and temperature dependent, and most important, also strongly dependent on dopant concentration, i,e., the average spacing between the hopping sites which are well identified in these materials. As dopants, electron accepting molecules (with strong electron affinity) serve as the hopping sites in electron conductors, while donor molecules (with low ionization potential) serve as the hopping sites in hole conductors. Thus the negative and positive charge carriers are of the form of an acceptor molecule with the additional electron or a hole as an ionized donor molecule, respectively. The low mobility is attributed to the residence time of the charge carrier, localized on the hopping site.

The polymer is essentially inert, providing a dielectric matrix to support the hopping sites. The hopping sites can be expected to retain most of the molecular properties of the dopant molecule. It is therefore useful to have a clear picture of the isolated dopant molecule if we are to understand the basic hopping process. We report here on the molecular orbital (MO) calculations on a model dopant for hole conduction, triphenylamine (TPA), which was chosen for its relative simplicity and symmetry. It and its close relative, tri-tolylamine (TTA), have also been investigated by the transient drift mobility technique.[3c,5,6]

Computational Details and Results

Ab initio calculations were performed using the Mulliken computer code,[7] using IBM RISC 6000 computers. Hartree–Fock (HF) calculations were performed using the 3-21G basis set.[8] Harmonic vibrational frequencies were calculated by differentiation of the energy gradient at the optimized geometries. No imaginary frequencies were computed at minima.

The optimized geometries for both the neutral and hole (radical cation) triphenylamine (TPA) molecules are presented in Fig. 1 and Table 1. The optimized geometry of the neutral molecule compares favorably with previous geometries obtained of the crystals.[8] Both the neutral and hole molecules have C_3 symmetry, and all the valence angles involving the C2, N10, C13, and C14 atoms are 120°, indicating NC_3 is planar. The TPA molecule can be visualized as a propeller, consisting of three blades of phenyl rings, as shown on the right side of Fig. 1. The axis goes through the central nitrogen perpendicular to the NC_3 plane. The pitch of the blade is about 43.5° for the neutral TPA. In going from the neutral to the hole geometry, the main change in the bond distances is in the elongation of the N–C bond by about 0.003 Å and contraction of the C–C bond on the sides of phenyl group by about 0.003 Å, while the pitch of the phenyl planes decreases by about 4° to about 39.2°.

While it is not entirely clear that the level of theory used may reliably predict, for example, a 0.003 Å change in a C–N bond length, nevertheless, one may say with a reasonable degree of certitude that the structural changes that occur upon ionization of TPA are very small. Consequently, the portion of the barrier for hole transport that is related to structural changes is also very small. The energy requirements associated with the neutral to hole changes in geometry are discussed below.

Orbital plots of the highest occupied molecular orbitals

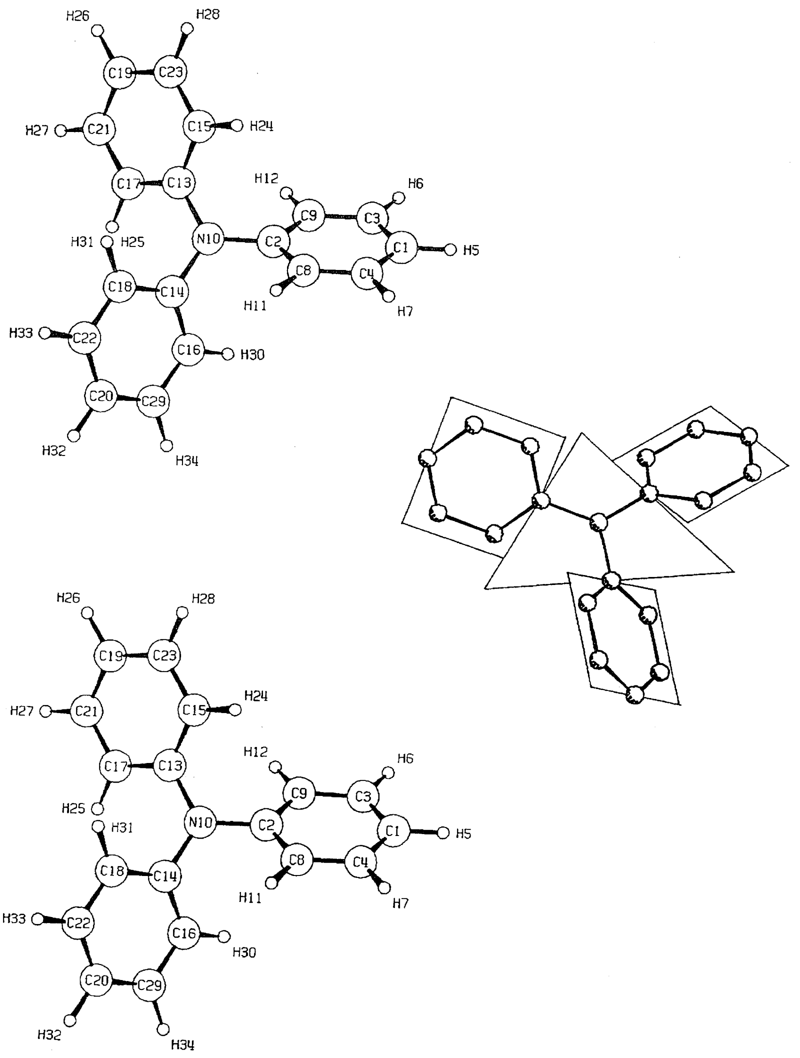

Fig. 1. The HF/3-21G optimized geometries for the neutral (top) and hole (bottom) geometries of TPA. The total energies are −740.669285324 and −740.442595241 hartrees for the neutral and hole geometries, respectively.

(HOMO) in both the TPA neutral and hole molecules, Fig. 2, are also topologically similar. The distribution of spin density due to the unpaired electron in the TPA hole indicates that 59% is localized on the nitrogen atom and most of the remainder on the various carbon atoms of the benzene rings. Hence, the delocalization of spin extends to the outermost carbon of the phenyl ring. The computed dipole moment for the neutral molecule is 0.002 Debye. A previously measured dipole moment for neutral TPA is 0.7 Debye.[10)]

The Frank–Condon principle[11)] is involved in the electron transfer that takes place when a hole hops to an adjacent hopping site. It is therefore of interest to determine the relative energies of the molecules in the two optimized geometries, the neutral molecule and the ionized (hole) molecules. This is plotted in Fig. 3. The instant the electron is separated from the neutral TPA molecule, the total energy of the ionized TPA and the separated electron while the geometry is that of the neutral TPA is 6.25 eV. The ion subsequently relaxes and the total energy is reduced by 0.08 eV to 6.17 eV. When such an ion accepts an electron, the neutral TPA, still in the relaxed ionized geometry, has an energy 0.07 eV higher than that of the relaxed neutral molecule.

Another result of interest from the computation is the vibrational modes. A description for the vibrational modes and their associated frequencies are summarized in Table 2 for the major absorption bands. The computed spectra are displayed in Fig. 4 using Lorentzian curves centered at the uniformly scaled (0.90) computed harmonic band centers, with a constant width at half height of 4 cm^{-1}. The uniform scaling corrects in part for the lack of a correlation treatment and anharmonicity effects.

Discussion

The hopping process responsible for conduction in the MDP has many aspects of the high temperature small polaron in molecular crystals discussed by Holstein.[10)] In terms of a simple hopping process involving the electron transfer between a neutral TPA molecule and an ionized TPA, the energy difference of the system, due to the Frank–Condon principle,[11)] is the sum of the energy difference between the neutral and ionized TPA geometry, i.e., 0.07+0.08 eV=0.15 eV.

Table 1. Optimized Parameters for Triphenylamine Neutral (RHF/3-21G) and Hole (ROHF/3-21G)

Length angstroms	Neutral	Hole	Angle (deg)	Neutral	Hole
C1C3	1.384	1.386	H5C1C3	120.36	119.83
C1C4	1.384	1.386	H5C1C4	120.36	119.83
C3C9	1.382	1.379	C1C4H7	120.06	120.22
C4C8	1.382	1.379	C1C4C8	120.49	120.14
C2C8	1.390	1.392	C1C3H6	120.07	120.23
C2C9	1.390	1.392	C1C3C9	120.50	120.14
C2N10	1.422	1.426	C3C9H12	120.33	120.52
N10C13	1.422	1.425	C3C9C2	120.33	119.29
N10C14	1.422	1.426	C4C8H11	120.33	120.52
C13C17	1.390	1.392	C4C8C2	120.34	119.29
C13C15	1.390	1.392	C8C2C9	119.05	120.80
C17C21	1.382	1.379	C8C2N10	120.47	119.60
C15C23	1.382	1.379	C9C2N10	120.48	119.60
C19C21	1.384	1.386	C2N10C13	120.00	120.00
C19C23	1.384	1.386	C2N10C14	120.00	120.00
C14C16	1.390	1.392	N10C13C15	120.48	119.60
C14C18	1.390	1.392	N10C13C17	120.48	119.60
C16C29	1.382	1.379	C13C15H24	119.33	120.18
C18C22	1.382	1.379	C13C15C23	120.34	119.29
C20C22	1.384	1.386	C13C17H25	119.33	120.18
C20C29	1.384	1.386	C13C17C21	120.33	119.29
C1H5	1.072	1.071	C15C23C19	120.49	120.14
C3H6	1.072	1.070	C15C23H28	119.44	119.63
C4H7	1.072	1.070	C17C21C19	120.50	120.15
C8H11	1.070	1.070	C17C21H27	119.43	119.63
C9H12	1.070	1.070	C21C19H26	120.36	119.83
C15H24	1.070	1.070	C23C19H26	120.36	119.83
C17H25	1.070	1.070	N10C14C16	120.48	119.60
C21H27	1.072	1.072	N10C14C18	120.48	119.60
C23H28	1.072	1.070	C14C16H30	119.34	120.18
C19H26	1.072	1.071	C14C16C29	120.33	119.29
C16H30	1.070	1.070	C14C18H31	119.33	120.18
C18H31	1.070	1.070	C14C18C22	120.34	119.28
C22H33	1.072	1.070	C16C29H34	119.43	120.14
C29H34	1.072	1.070	C16C29C20	120.50	120.14
C20H32	1.071	1.071	C18C22H33	119.44	119.63
			C18C22C20	120.49	120.14
			H32C20C22	120.36	119.83
			H32C20C29	120.36	119.83
			C13N10C14	120.00	120.01

Dihedral Angle	Neutral	Hole
N10C2C8C4	179.6	−179.63
C13C10C2C9	−43.56	−39.24
C14C10C2C9	136.45	140.76
C14N10C2C8	−43.57	−39.24
C15C13C10C2	−43.65	−39.19
C18C14N10C2	136.38	140.79

The actual case of MDP is further complicated by the fact that the material is set in an amorphous polymer matrix. There is the contribution from the dielectric polarization of the polymer matrix. The orientation of the nearest neighbor TPA molecules and the average separation are different. The steric environment of each TPA molecule is also different, leading to slight variations in the molecular structure.

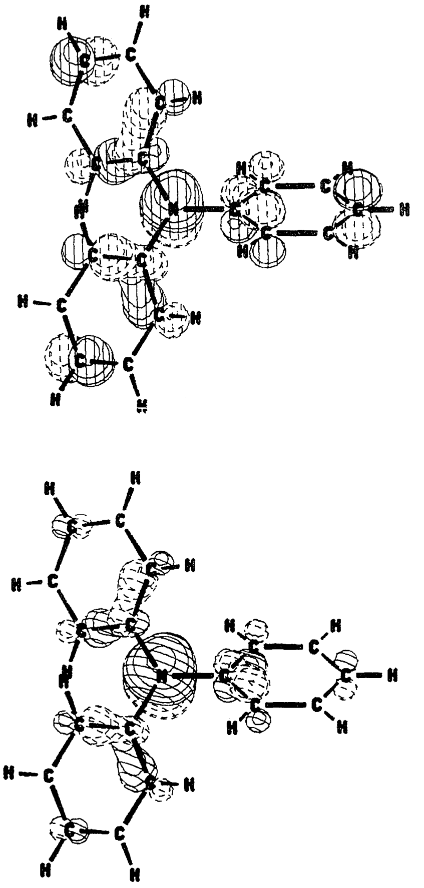

Fig. 2. The highest occupied molecular orbitals for the (top) neutral and (bottom) hole geometries.

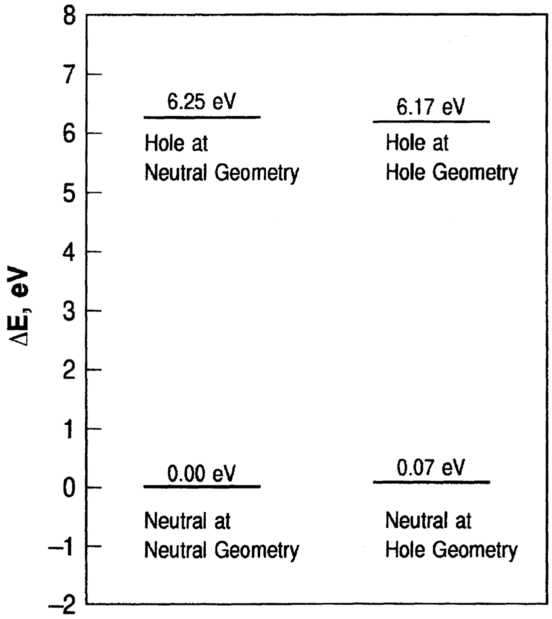

Fig. 3. The relative energies versus geometries for the TPA neutral and hole molecules.

The hopping is thermally activated, so that the vibrational mode of the TPA molecule interacting with the phonons will play a role. The two most striking differences in the infrared spectrum of the hole, compared to the neutral, are a decreases

Table 2. A Description for the Vibrational Modes and Associated Frequencies for the Major Infrared Bands Computed for the TPA Neutral and Hole Molecules

Vibrational mode	Frequencies (cm^{-1})	
	Neutral	Hole
C–H stretch	3044	3060
Ring C–C stretch	1590, 1504	1573, 1467
C–H in plane bend	1362	1362, 1085, 1018
C–N stretch	1263	1164, 1132
C–H out of plane bend	802, 730	805, 716
C–H out of plane bend+ring C–C bend		899
N out of plane deformation+ring deformation	639, 521	638

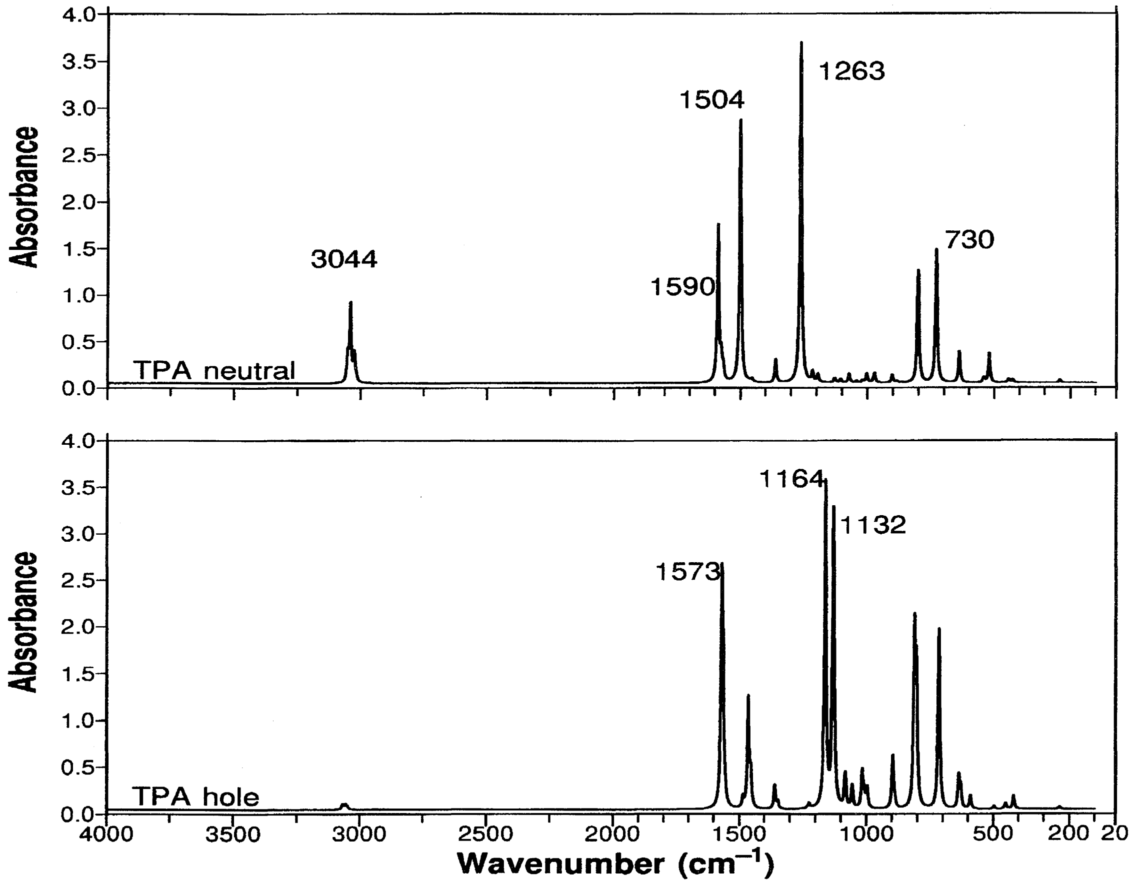

Fig. 4. The HF/3-21G computed infrared spectra of the (top) neutral and (bottom) hole TPA molecules.

in the intensity of bands in the C–H stretching region, ≃ 3000 cm^{-1}, and a ≃ 100 cm^{-1} shift to lower frequencies of the C–N stretching bands. The computed normal mode vectors for the 1164 and 1132 cm^{-1} C–N stretching vibrations in the hole are presented in Fig. 5. As indicated in the figure, the 1132 cm^{-1} band is a mixture of both C–N stretch and an in-plane C–H bend. Based upon the changes in the infrared spectrum, the accompanying vibration upon hole formation appears to be dominated by a C–N stretching vibration. Although we do not have any direct evidence that these vibrational modes are involved in the mechanism for the hole transport, we stress that the barrier for the TPA neutral to hole conversion, 0.15 eV, is about the energy of the C–N vibrational modes. Also, the C–N stretching motion couples the charge on the nitrogen atom with the phenyl rings, and if we view the transport mechanism as movement of charge from phenyl rings on neutral to phenyl rings on charged TPA (In an MDP amorphous environment phenyl rings are more likely to be in contact) then charge may flow from nitrogen on neutral TPA to nitrogen on TPA hole via adjacent phenyl groups. In summary, the optimized geometries for both the TPA neutral and hole molecules indicate a modest geometric change upon hole formation. The energy barrier associated with formation of the hole geometry at the fully occupied state is 0.15 eV, consistent with vibrational energies. The computed infrared spectra indicate the accompanying modes of both the neutral and ionized TPA.

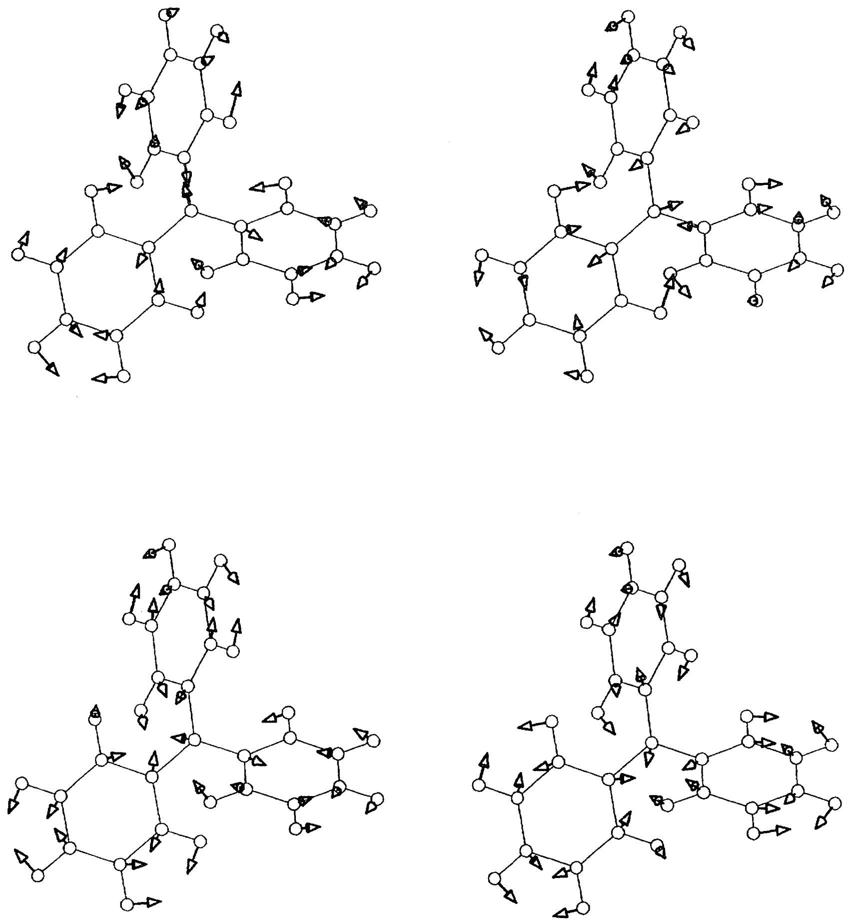

Fig. 5. The computed normal mode displacement vectors for the 1164 cm^{-1} (top two figures) and the 1132 cm^{-1} (bottom two figures) frequencies.

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