Aromatic Amines: A Comparison of Electron-Donor Strengths

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Received: August 4, 2005

The electron-donor abilities of ten aminophenyl systems and an additional aminothienyl system are compared using density functional theory calculations. The systems studied here include those with amine nitrogen atoms bearing alkyl or aryl groups and those with amine nitrogen atoms as part of a heterocycle. Their abilities to act as donors in electron-transfer processes are assessed from calculated vertical ionization potentials for the aminobenzenes, which are in good agreement with available experimental data. Their abilities to act as intramolecular π-electron donors in conjugated systems are inferred from the bond lengths and charge densities calculated for the corresponding 4-aminobenzaldehydes and 4-aminobenzonitriles. The computed ^{13}C NMR chemical shifts for the 4-aminobenzaldehydes and 4-aminobenzonitriles are in good agreement with published and new experimental data. The chemical shifts correlate well with the computed charge densities and can, to some extent, be used as an experimental probe of π-donor strength. We find that the electron-transfer-donor strengths do not correlate well with π-donor strengths: these differences can largely be attributed to steric effects.

Introduction

Amines are widely used as electron donors in organic materials chemistry. For example, donor−(π-conjugated bridge)−acceptor (D−π−A) chromophores for second-order nonlinear optical (NLO) applications almost invariably contain a 4-(diakylamino)- or 4-(diarylamino)phenyl donor group.[1,2] Some amine-containing organic chromophores also have interesting third-order NLO properties including efficient third-harmonic generation.[3] Recently, molecules with amine donors incorporated into D−π−D, D−A−D and D−π−A motifs have been shown to exhibit large two-photon absorption cross-sections,[4,5] which have been exploited for a variety of applications.[6] In addition, amines, in particular, 4,4′-bis(diarylamino)biphenyl (TPD) derivatives,[7] are widely used as hole-transport materials for applications including xerography,[8] organic light-emitting diodes,[9] and photorefractives.[10]

Many different amine-based donors have been used in these applications; typically, structural variations have been made to improve solubility, or the thermal or photostability of the chromophores. For example, it has been shown that D−π−A second-order NLO dyes display enhanced stabilities when 4-(dialkylamino)phenyl donors are replaced with 4-(diarylamino)phenyl groups.[11,12]

Interestingly, there have been only a few attempts to systematically compare the relative donor abilities of these and other amines, with most comparisons including only a handful of species.[2,5,12−16] Surprisingly, the distinction between the ability to act as an electron donor in an intermolecular electron-transfer (ET) reaction, which we will refer to as the ET-donor strength, and to act as an intramolecular electron donor toward a conjugated π-system, the π-donor strength, does not seem to have been explicitly discussed in the context of amines.[17] The ET-donor strength can be related to the HOMO energy or the ionization potential (IP) of a molecule and is relevant to hole injection from electrodes, or from other organic materials, and in applications involving ground-state or photoinduced electron transfer.[18] On the other hand, the π-donor strength depends on not only the HOMO energy of an amine donor group but also the extent to which this orbital can couple to the orbitals of a conjugated π-system. The π-donor strength plays an important role in determining NLO properties. For example, it has been shown that in D−π−A chromophores, the second- and third-order molecular polarizabilities, β (responsible for phenomena such as frequency doubling and the electrooptic effect) and γ (frequency tripling, four-wave mixing, intensity-dependent refractive index), are critically dependent on the degree of bond-length alternation (BLA) in the π-bridge; BLA, in turn, depends on the relative energies of the neutral and charged-separated resonance structures (see Figure 1) and, hence, on the strength of the π-donor.[19]

In this contribution, we provide a consistent comparison of ten 4-aminophenyl donor systems, **1**−**10** (Chart 1). We also compare these amines with a representative example from the class of 2-(5-aminothienyl) donors, **11**, because the latter have attracted attention as alternatives to 4-aminophenyl donors for second-order NLO applications.[2,20]

The abilities of **1**−**11** to act as donors in intermolecular electron-transfer (ET) reactions are determined by comparison of the vertical ionization potentials (IPs) of the parent amines, **1a**−**11a**, obtained from density functional theory (DFT) calculations. Their abilities as intramolecular π-donors in conjugated systems are assessed by considering simple model D−A species. Specifically, we chose to examine bond lengths, atomic charge densities, and NMR parameters in the aldehyde, **1b**−**11b**, and the nitrile, **1c**−**11c**, derivatives of the parent amines. Where available, experimental IP and NMR data are compared with the calculations. To expand the range of the comparison, we have included NMR data for three new aldehydes, **9b**−**11b**, that we have recently synthesized.

10.1021/jp054334s CCC: $30.25

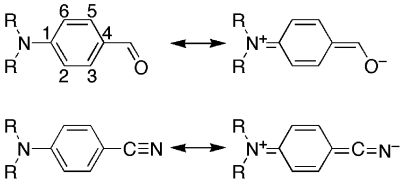
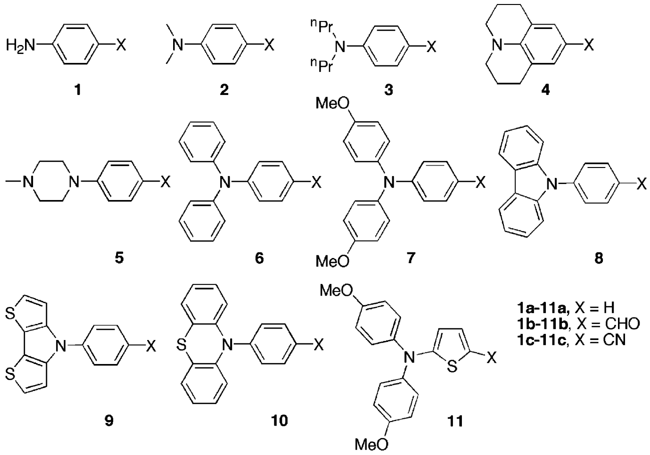


Figure 1. Neutral and charge-separated resonance structures for simple donor−acceptor compounds. The numbering of the phenyl carbon atoms used in the text and subsequent figures is also shown.

CHART 1: Parent Amines, 1a−11a, Aldehydes, 1b−11b, and Nitriles, 1c−11c, Considered in This Study



Computational Details

The molecular geometries of all compounds were fully optimized at the DFT-B3LYP/6-311G(d,p) level[21] without imposing any symmetry constraints. All results quoted in the main body of the paper are based on calculation using the B3LYP functional, which is currently the most widely used DFT functional and is known to perform well in terms of geometries and energetics.[22] However, because the variations in ionization potentials (IPs) and bond lengths between different amines are rather small (bond-length differences of ca. 0.001 Å in some cases), we also tested two other well-known DFT functionals (B3PW91 and PBE1PBE)[22] for a limited set of molecules (**1c**−**4c**) to check whether the trends we observe are robust. Though IPs varied a little ($\leq$0.04 eV) depending on the method, these variations are less than the differences in IP between the different molecules and, more importantly, the trends between different molecules are consistent using the different methods (see Supporting Information, Figure S1). Bond lengths vary with the method by as much as 0.01 Å, i.e., by more than some of the differences between bond lengths in different molecules; however, the *trends* in molecules are reproduced extremely well from method to method (as shown in the Supporting Information, Figure S2). These results strongly support the reliability of the trends in electron-transfer-donor strengths and π-donor strengths discussed below.

Vertical ionization potentials (IPs) were calculated by subtracting the total energy of the neutral molecule from that of the charged molecule at the neutral equilibrium geometries. Natural population analysis (NPA)[23] was carried out to compute atomic charges.[24] Chemical shifts were calculated by using the gauge-independent atomic orbital (GIAO) method[24,25] at the DFT-B3LYP/6-311+G(2d,p) level based on the B3LYP/6-311G(d,p) optimized geometries. All calculated ^{13}C, ^{15}N, and ^{17}O shielding values were referenced to the calculated absolute shielding of $SiMe_4$, CH_3NO_2, and H_2O, respectively ($\sigma_{rel} = \sigma_{ref} - \sigma_{abs}$).

TABLE 1: Calculated Vertical Ionization Potentials (eV) for Some Amines, Along with Literature Values from Gas-Phase Photoelectron Experiments for Comparison (in Italics)

	a series; X = H	**b** series; X = CHO		**c** series; X = CN	
amine	IP	IP	ΔIP[a]	IP	ΔIP[a]
1	7.75 *7.69*,[35] *7.70*,[36,37] *8.10*[31]	8.08	0.33	8.18	0.43
2	7.12 *7.14*,[35] *7.6*,[38] *7.45*[31,39]	7.46 *7.70*,[39] *7.81*[40]	0.34	7.57 *7.86*[41]	0.45
3	6.81[b]	7.22	0.41	7.32[b]	0.51
4	6.78 *7.05*[31]	7.09	0.31	7.20 *7.26*[41]	0.42
5	7.21	7.46	0.25	7.56	0.35
6	6.65 *6.86*[42]	6.97	0.32	7.07	0.42
7	6.20	6.57	0.37	6.66	0.46
8	7.08	7.30	0.22	7.39	0.31
9	7.07	7.31	0.24	7.39	0.32
10	6.68	6.87	0.19	6.97	0.29
11	6.23	6.55	0.32	6.62	0.39

[a] ΔIP is defined as the difference between the IP of the **b** or **c** series compound and that of the corresponding **a** series compound. [b] PES data have not been reported for **3a** or **3c**, but values of 7.20[31] and 7.65[41] eV have been reported for their respective diethylamino analogues.

Results and Discussion

Electron-Transfer (ET)-Donor Strength. We chose to calculate the vertical IPs as a measurement of the ET electron-donor strength because these can be directly compared to experimental data from gas-phase photoelectron spectroscopy (PES).[26] Table 1 shows values of IP for **1a**−**11a**, **1b**−**11b**, and **1c**−**11c** according to DFT calculations at the B3LYP/6-311G** level, along with literature PES values where available. In general, the calculations reproduce the experimental values well within the relatively large variations seen between different experimental data sets. More importantly, the computed values reproduce trends between different molecules investigated in the same experimental study.[27] In addition, the trends are in good agreement with those evident among other experimental values of IP. For example, IPs of donors can be estimated from the absorption in intermolecular charge-transfer complexes formed with acceptors; one such study estimates the IPs of **2a** and **3a** as 7.3 and 7.15 eV, respectively,[28] and another gives values of 7.76, 7.44, and 6.96 eV for **1a**, **2a**, and **3a**, respectively.[29] A mass spectrometric method led to values of 8.64 and 7.99 eV for **1c** and **2c**.[30]

The data clearly show triarylamines (**6a** and **7a**) to be more readily ionized than their *N*,*N*-dialkylanilines analogues (**2a**−**5a**). The (dialkylamino)phenyl data show, in agreement with experimental IP data,[28,29,31] that longer alkyl chain lengths lead to lower ionization potentials. This effect seems to be more important than geometrical effects induced by the fused rings in determining the differences in the IPs of *N*,*N*-dimethylaniline (**2a**) and julolidine (**4a**), because our calculations show *N*,*N*-di-*n*-propylaniline (**3a**) and julolidine (equal length alkyl chains) to have similar IPs.

N-Phenylcarbazole (**8a**) is somewhat more difficult to ionize than triphenylamine (**6a**); this can be attributed to the large twist angle between the carbazole unit and the phenyl group in **8a** (ca. 60°), which leads to less delocalization of the HOMO into the phenyl ring.

We were also interested in *N*-phenyldithienopyrrole (**9a**) as an alternative donor: because thiophene is more easily ionized than benzene,[32] one might anticipate that the dithienopyrrole heterocycle would have a much higher HOMO energy than carbazole. Moreover, reduced steric hindrance in **9a** between the phenyl group and the heterocycle might be anticipated to

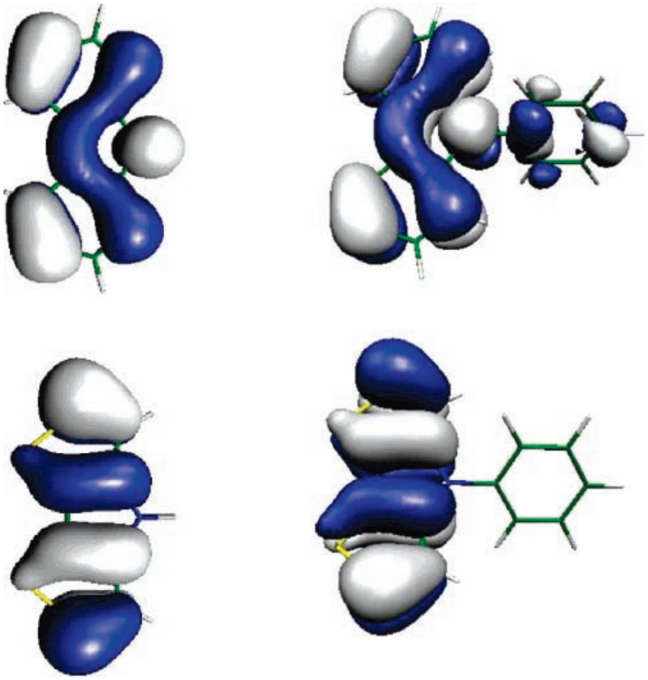


Figure 2. HOMOs from DFT calculations for carbazole (upper left), dithienopyrrole (lower left), and their *N*-phenyl derivatives, **8a** (upper right) and **9a** (lower right).

lead to a reduced torsion and better delocalization of the HOMO over both heterocycle and phenyl rings. Though the calculated IP in the parent dithienopyrrole (7.16 eV) is indeed lower than in carbazole (7.40 eV[33]), and the torsion angle between the heterocycle and phenyl rings in **9a** is somewhat reduced (45.5°) relative to that in **8a** (ca. 60°), the calculated IPs for **8a** and **9a** are rather similar. The reason for this can be seen by examining the HOMOs of **8a** and **9a**, which are shown in Figure 2, along with those of the parent heterocyclic units. The HOMO of **8a** can be described as an antibonding combination of an orbital similar to the HOMO of carbazole and a phenyl-based π-orbital; the energy of this orbital is raised relative to that of carbazole itself through this carbazole−phenyl interaction. In contrast, the HOMO of **9a** is essentially the same as in dithienopyrrole. The HOMOs of **9a** and dithienopyrrole can both be regarded as antisymmetric combinations of the local HOMOs of the two thiophene fragments, with the nitrogen atom lying on a nodal plane; the location of the nodal plane in this orbital precludes overlap between the HOMOs of the phenyl and dithienopyrrole fragments in the **9a** HOMO. Thus, the similar IPs of **8a** and **9a** are due to the effects of a higher energy HOMO for the dithienopyrrole fragment being essentially canceled by the lack of phenyl contributions to the HOMO of **9a**.

Compound **10a**, *N*-phenylphenothiazine, is even more severely twisted, with a dihedral angle of 81.6° between the mean planes of the puckered phenothiazine ring system and the phenyl group; this sterically induced twist can be held responsible for the lack of phenyl contributions to the HOMO that we also observe in this molecule.[34]

In summary, the calculated IPs for **1a**−**11a** vary over a range of ca. 1.5 eV. Aniline itself (**1a**) is the most difficult to ionize. *N*,*N*-bis(4-methoxyphenyl)aniline (**7a**) and 2-(*N*,*N*-bis(4-methoxyphenyl)amino)thiophene (**11a**) are the most readily ionized.

***π*-Donor Strength: C−X Bond Lengths.** Although IPs provide a measure of the ET-donor strength, they do not necessarily correlate with the ability of the donor to couple to a π-system, i.e., with the π-donor strength. We have investigated π-donor strengths by examining simple models for D−π−A species: the amines **1a**−**11a** substituted with formyl (**1b**−**11b**) and cyano acceptors (**1c**−**11c**).

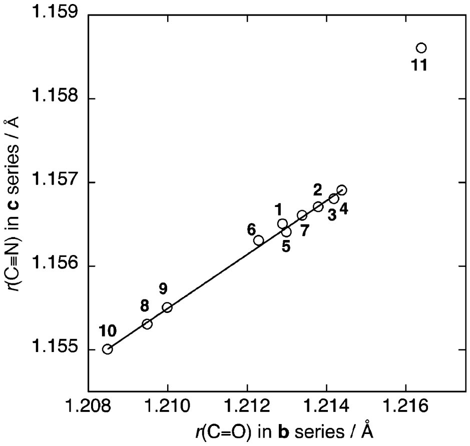


Figure 3. Calculated C≡N bond lengths for the nitriles **1**−**11c** plotted against the calculated C=O bond lengths for the corresponding aldehydes, **1**−**11b**. The line is a least-squares fit to the data for **1**−**10b** and **1**−**10c**.

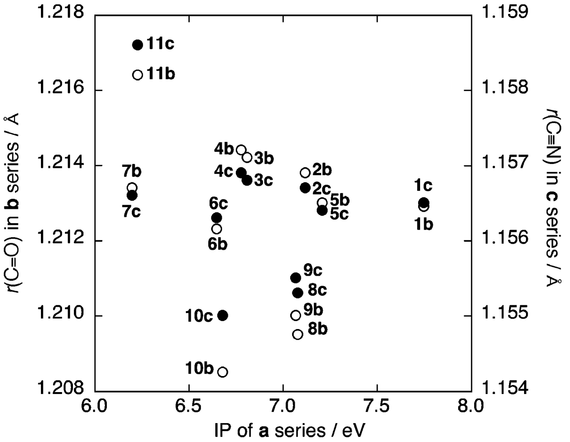


Figure 4. Calculated C=O bond lengths in the aldehydes, **1**−**11b** (open circles), and calculated C≡N bond lengths for the corresponding nitriles, **1**−**11c** (filled circles), plotted against the calculated vertical IPs of the parent amines, **1**−**11a**, showing the poor correlation between ET-donor and π-donor strength.

As a fundamental measure of the relative contributions of the neutral and zwitterionic resonance forms (Figure 1), we have examined the bond lengths within the aldehydes, **1b**−**11b**, and nitriles, **1c**−**11c**. Figure 3 compares the calculated carbonyl C−O and nitrile C−N bond lengths in **1b**−**11b** and **1c**−**11c**, respectively; in each series, a longer C−Z bond reflects greater contributions from the charge-separated structure and, hence, a stronger donor. The figure clearly shows that one obtains essentially the same ordering of π-donor strengths from both C−O or C−N bond lengths, and that the relationship between the aldehyde C−O and nitrile C−N bond lengths is linear if one excludes the thiophene compounds **11b** and **11c**.

The order of π-donor strengths (indicated by the bond lengths of Figure 3) is clearly different from that of ET-donor strengths (as indicated by the IP data of Table 1). The general lack of correlation between the two types of donor strengths in systems **1**−**11** is emphasized in Figure 4, where the horizontal axis is a measure of ET-donor strength and the vertical axis is a measure of π-donor strength. The correlation between the bond lengths in the acceptor groups and ΔIP, defined as the difference in IP between the aldehydes or nitriles and the corresponding parent amines, is also poor (Figure S3 in Supporting Information).

For example, the 4-(diphenylamino)phenyl group is clearly seen to be a poorer π-donor in **6b** and **6c** than the 4-(dimethylamino)phenyl group in **2b** and **2c**, despite the parent triphenylamine (**6a**) being a better ET-donor than *N*,*N*-dimethylaniline (**2a**). Our results are consistent with previous studies of D−A species that also suggest 4-(dialkylamino)phenyls to be stronger π-donors than 4-(diphenylamino)phenyl on the basis of the energy of the visible low-energy charge-transfer absorptions[2,5,12] and on ^{1}H NMR data (δ_{CHO} of aldehydes).[15] One possible reason for this difference in π-donor strengths is a steric effect; in the **6** system there is a dihedral angle, ψ, of ca. 40° between the plane of the C_6H_4X ring and the plane formed by the N atom and the two attached carbon atoms of the terminal R groups, whereas the corresponding angle in the **2** system is close to zero. To examine the effect of this twist upon the π-donor strength, we also optimized the structures of **2b** and **c** with the value of ψ constrained to that found in **6b** and **c**, respectively: the resulting C−O and C−N bond lengths in the acceptor groups are shorter than in fully optimized **2b/c** and approach those in **6b/c**. Similarly, we optimized **6b/c** with ψ constrained to the value for **2b**/**c** and the acceptor C−O and C−N bond lengths approached those seen in **2b/c**. This confirms that the difference in π-donor strength is indeed primarily due to the sterically induced twisting in the triarylamine system.

The calculated bond-length data for **7b** and **7c** show that replacement of the terminal phenyl groups with *p*-methoxyphenyl groups leads to a π-donor strength closer to that of 4-(dimethylamino)phenyl (**2**) than to that of 4-(diphenylamino)phenyl (**6**). Because materials incorporating 4-(diarylamino)phenyl donors are often more stable than their 4-(dialkylamino)phenyl analogues,[11,12] **7** may, therefore, for many applications represent a useful compromise between the relatively unstable, but strongly π-donating, dialkylamino systems (**2**−**5**) and the more stable, but more weakly π-donating, triarylamine system (**6**).

Despite the general lack of correlation between π- and ET-donor strengths discussed above, some patterns are discernible in Figure 4: the π-donor strengths for the 4-(dialkylamino)benzaldehydes, **1b**−**4b**, and 4-(dialkylamino)benzonitriles, **1c**−**4c**, parallel the ET strengths of the analogous *N*,*N*-dialkylanilines, **1a**−**4a**; the increase in π-donor strength with alkyl chain length (**2a** vs **3a**) is consistent with previous inferences drawn from UV−vis absorption maxima of various D−π−A[2] and D−A−D systems;[16] and the different π-donor strengths of systems **1** and **2** have previously been seen in calculated geometries of simple D−A systems, including **1c** and **2c**,[14] and in the absorption maxima of the 4-(tricyanovinyl)anilines.[13] The **5** system appears somewhat anomalous among the *N*,*N*-dialkylanilines; although **5** has a similar ET-donor strength to **2**, the π-donor strength of the **5** system is comparable to that of the **1** system.

As with the ET-donor strength (vide supra), the π-donor strength of 4-julolidinyl, **4**, is similar, although slightly higher, than that of 4-(di-*n*-propylamino)phenyl, **3**, and significantly higher than that of 4-(dimethylamino)phenyl, **2**, suggesting that the differences in π-donor strength between **2** and **4** are principally due to the longer groups attached to the amine nitrogen atom in the latter case. However, we cannot rule out that in experimental comparisons of **2** and **4**, for example, in comparisons of absorption maxima of D−A derivatives,[13,43] the rigidization imposed by the ring fusions in **4** may be important in preventing thermal population of torsional modes through which the π-donor strength of **2** may be reduced.

Our results on the *N*-phenylcarbazole, **8**, system are consistent with previous work (based on ^{1}H NMR spectra of aldehydes and on the calculated geometries of stilbazolium derivatives) that has suggested **8** to be a weaker π-donor than the **6** system.[15] The other two fused-ring donor systems, **9** and **10**, are also rather poor π-donors despite moderate ET-donor strengths. Though the good conjugation within the fused-ring section of the **8**−**10** systems leads to moderate IPs, steric influences (and, in the case of **9**, the HOMO localization away from the nitrogen atom) effectively reduce the conjugation between the fused ring and the phenyl group, leading to little or no HOMO density on the phenyl group.

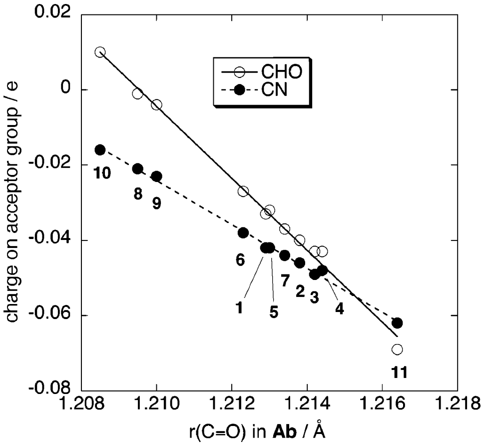


Figure 5. Calculated NPA charges on the CHO and CN acceptor groups of **1b**−**11b** and **1c**−**11c**, respectively, plotted against the C−O bond lengths in **1b**−**11b**.

Finally, comparison of the data for the **7** and **11** systems in Figures 3 and 4 shows that replacing the *para*-phenylene between the donor nitrogen and the acceptor with 2,5-thienylene leads to a considerable increase in π-donor strength; indeed, the difference in the C−Z bond lengths of the **7** and **11** systems is over half that between the strongest and weakest π-donating aminophenyl species (**4** and **10)** systems. This can be attributed to a combination of the lower IP[32] and reduced aromaticity of thiophene[44] relative to benzene.

Other Measures of π-Donor Strength. In addition to the C−O and C−N bond lengths in the acceptors, other bond lengths may be used as measures of amine π-donor strength. The C4−C_{CN} and C4−C_{CHO} bond lengths decrease smoothly as the C−O bond length increases (see Figure S4 in the Supporting Information) and, if **11b** and **11c** are excluded, the correlation is linear. The BLA in the phenylene groups of **1b**−**10b** and **1c**−**10c**[45] also increases in a more-or-less linear fashion with increasing C−O bond length in **1b**−**10b** (Figure S5); the most conspicuous outliers from the plot are the julolidine derivatives, **4b** and **4c**, in which geometric constraints are imposed on the phenylene ring by the fused saturated groups. The N_{amine}−C1 bond lengths do not correlate particularly closely with the C−O bond length (Figure S5); however, this particular bond is likely to be affected by steric effects at the amine nitrogen, in addition to depending upon the degree of π-donation.

As well as changes in bond lengths, one also expects the charge associated with the acceptor group to vary from donor to donor in the series **1b**−**11b** and **1c**−**11c**.[46] This is indeed the case; Figure 5 clearly shows that the natural population analysis (NPA) charges on the CHO and CN acceptor groups become more negative with increasing C−O bond length in the aldehydes, **1b**−**11b** (similar plots are obtained if the charge data are plotted against the cyanide C−N bond length for **1c**−**11c**). In addition, if data for the julolidine derivatives, **4b** and **4c**, where alkyl, rather than hydrogen, substituents occupy the 2,6

TABLE 2: Calculated and Experimental[49,50] (CDCl$_3$) NMR Data for 1b−11b and 1c−11c[a]

	δ_{calc}/ppm						δ_{expt}/ppm				
	C1	C2,6	C3,5	C4	CZ	Z	C1	C2,6	C3,5	C4	CZ
1b	159	117	138	135	192	595					
2b	158	114	138	133	193	591	154.32	110.98	131.87	125.10	190.26
3b	158	114	138	132	192	586					
4b	153	126	136	133	192	586					
5b	162	119	138	135	193	598	155.20	113.30	132.00	126.10	190.40
6b	161	126	136	137	193	604	153.41	125.11	131.26	129.30	190.26
7b	161	123	138	135	192	596	154.10	116.90	131.50	127.90	190.30
8b	152	133	137	141	194	627					
9b	153	128	138	140	194	623	144.80	121.80	131.60	133.40	190.80
10b	156	142	138	143	195	637	150.96	119.96	131.60	130.36	190.61
11b	177	117	135	142	182	574	166.19	109.09	138.83	128.65	180.95
1c	156	117	141	107	124	−116	150.93	114.41	133.72	99.360	120.48
2c	156	115	140	105	125	−116	152.46	111.40	133.27	97.120	120.72
3c	156	114	140	104	124	−117					
4c	151	127	139	105	114	−119					
5c	160	119	140	108	124	−115	152.94	113.76	133.00	99.530	119.68
6c	159	126	140	110	124	−114	151.56	125.11	133.16	102.47	119.70
7c	159	123	140	108	123	−116					
8c	150	132	140	117	124	−109					
9c	151	128	141	115	123	−110					
10c	154	143	139	120	123	−108					
11c	174	114	142	107	119	−105					

[a] Positions defined in Figure 2; Z is the CHO ^{17}O shift for **1b−11b** and the CN ^{15}N shift for **1c−11c**.

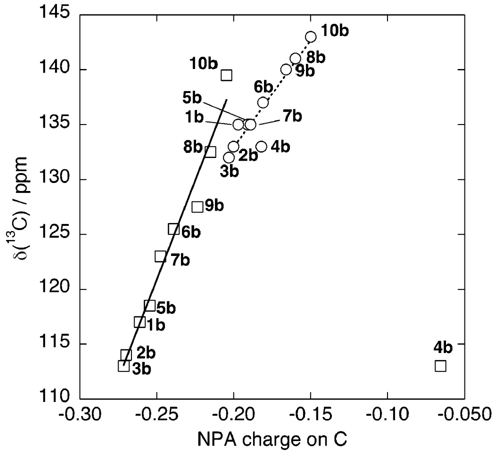


Figure 6. Correlation between NPA charge and ^{13}C NMR shifts for the 2,6 (squares, solid line) and 4 (circles, dashed line) C positions of the aldehydes **1b−10b**. The point representing the 2,6 positions of **4b** is omitted from the fit because these particular C atoms bear σ-electron-donating alkyl groups and so the differences between this NPA charge and those for the other compounds do not depend only on the differing π-effects of the amine donor (presumably some inductive effects are operative to a less degree on the C4 atom).

positions, are excluded, the charges on the C2, C4, and C6 atoms of the phenylene groups of the D−A compounds, **1b−10b** and **1c−10c**, also vary with the C−O bond length in a reasonably linear fashion (shown in Figure S6 for **1b−10b**). However, the order of π-donor strengths that would be deduced from the charges on aryl C atoms is slightly different from that deduced from C−Z bond lengths or charges (the positions of **6** and **1**/**5**, fairly close according to either measure, are reversed). The charges on the carbon atoms in the remaining positions of the phenylene ring are much less sensitive to the π-donor strength; this is to be expected because it is possible to write sound resonance structures in which the amine nitrogens carry a positive charge and the 2, 4, or 6 positions carry a negative charge, but not to write reasonable structures in which the negative charge is located on the 1, 3, or 5 positions.

^{13}C NMR Data. Finally, we compare the results of our calculations with an experimental probe of π-donor strength. We note that the bond-length changes discussed above are rather subtle to be detected reliably by crystallography; in addition, crystallographic data are not available for a very wide range of compounds.[47] However, the NMR chemical shifts of ^{13}C nuclei are known to be correlated to the π-electron density at that carbon,[48] and in many cases experimental data[49] are available for us to compare with our computed values. Hence, we have calculated the ^{13}C NMR chemical shifts for **1b−11b** and **1c−11c**. Table 2 compares our computed shifts to literature data and to new ^{13}C NMR data we have acquired (on **7b** and on the new compounds **9−11b**) to expand the range of the comparison.[50] In addition, we have calculated ^{15}N and ^{17}O shifts for the heteroatoms; however, although the acceptor ^{17}O shifts in the aldehydes are rather sensitive to the identity of the donor, scant experimental data are available for comparison. The calculated ^{13}C shifts are in good agreement with experimental data; although the calculations, in which solvation is neglected, give ^{13}C chemical shifts ca. 5−10 ppm higher than experiment, the patterns of variation in chemical shifts from one ^{13}C position to another and from one compound to another are reproduced well. The ^{13}C shifts corresponding to the 2, 6, and 4 positions of the phenylene rings of **1−10b** and **1−10c** are those that are most sensitive to the identity of the donor, as expected from the NPA charge data. As shown for **1−10b** in Figure 6, the ^{13}C shifts for these positions do indeed correlate well with the charge densities on the relevant atoms. The ^{13}C shifts for the 1 and 3,5 positions, and for the carbon atom of the acceptor group itself are relatively insensitive to the identity of the donor.

We stress, however, that ^{13}C chemical shifts must be used with caution to infer relative π-donor strengths; as discussed above, the NPA charges on the 2,6 and 4 positions do not correlate precisely with the more direct measures of donor strength based on the bond length in, or the charge on, the acceptor group. Moreover, the presence of additional substituents on the phenylene ring (as in the **4** system) or the replacement of this ring with a heterocycle (as in the **11** system) also affects the chemical shift, independent of any effect on the acceptor group.

Conclusion

We have compared the electron-transfer-donor strengths and π-donor strengths of various amines by calculating their ionization potentials and, in combination with two different acceptor groups, the resulting bond-length patterns, atomic charges, and NMR chemical shifts. Though ET and π-donor strengths are correlated within limited groups of compounds (e.g., comparing one dialkylaniline against another), in general, the IP is a very poor guide to the ability of 4-aminophenyl groups to act as π-donors in conjugated organic molecules. For example, 4-(diphenylamino)phenyl is a weaker π-donor than 4-(dimethylamino)phenyl, despite the parent aniline having a lower IP in the first case. This difference can be largely attributed to steric effects.

The 4-[bis(4-methoxyphenyl)amino]phenyl group offers a promising combination of a reasonably high π-donor strength with the higher stability previously reported for 4-(diarylamino)-phenyl donors. 4-Aminophenyl derivatives in which the amine group is part of planar fused-ring heterocycles, such as carbazole, are shown to be rather poor π-donors due to steric effects and, in one case, due to orbital localization effects.

The strongest π-donor among those we have investigated is a 2-(5-diarylamino)thienyl group; the difference in π-donor strength between this and its 4-(diarylamino)phenyl analogue can be attributed to the reduced aromaticity of thiophene relative to benzene and is considerably more than the difference in strengths seen between the strongest 4-(dialkylamino)phenyl donor and the weakest 4-(diphenylamino)phenyl example.

We expect this study to act as a valuable guideline for the further design of hole-transport materials and NLO chromophores.

Acknowledgment. This material is based upon work supported in part by the STC Program of the National Science Foundation under Agreement Number DMR-0120967. The NSF (grant CHE-0343421) and the Office of Naval Research are also gratefully acknowledged. We thank Shijun Zheng for providing a sample of **7b** for ^{13}C analysis.

Supporting Information Available: Additional plots showing: comparison of IPs and selected bond lengths for **1c**−**4c** obtained using different DFT functionals; variation of the C−O and C−N bond lengths in **1b**−**11b** and **1c**−**11c** with the difference in IPs between these compounds and their parent amines, **1a**−**11a**; calculated C−CHO and C−CN bond lengths in **1b**−**11b** and **1c**−**11c** plotted against C═O bond lengths in **1**−**11b**; variation with C═O bond length in **1**−**11b** of bond-length alternation in the 1,4-substituted phenyl groups of **1**−**10b** and **1**−**10c**, and of N1−C1 bond lengths in **1**−**11b** and **1**−**11c**; and NPA charges on the C2,6 and C4 positions of the aldehydes **1b**−**10b** plotted against the C═O bond length for the same compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) The dipole moment is *not* a particularly useful measure of π-donor strength; although it is affected by the zwitterionic resonance contribution to the ground-state structure, it also depends on local contributions such as the dipoles associated with the thiophene rings of the **9** and **11** systems, and so does not correlate well with other measures.

(47) Crystal structures of some of the species considered in this paper have been determined: **1a** (Fukuyo, M.; Hirotsu, K.; Higuchi, T. *Acta Crystallogr.* **1982**, *B38*, 640); **1c** (Merlino, S.; Sartori, F. *Acta Crystallogr.* **1982**, *B38*, 1476. Heine, A.; Herber-Irmer, R.; Stalke, D.; Kühnle, W.; Zachariasse, K. A. *Acta Crystallogr.* **1994**, *B50*, 363); **2c** (Jameson, G. B.; Sheikh-Ali, B. M.; Weiss, R. G. *Acta Crystallogr.* **1994**, *B50*, 703. Heine, A.; Herber-Irmer, R.; Stalke, D.; Kühnle, W.; Zachariasse, K. A. *Acta Crystallogr.* **1994**, *B50*, 363); **8a** (Avendaño, C.; Espada, M.; Ocaña, B.; García-Granda, S.; del Rosario Díaz, M.; Tejerina, B.; Gómez-Beltrán, F.; Martínez, A.; Elgero, J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1547); **8c** (Saha, S.; Samanta, A. *Acta Crystallogr.* **1999**, *C55*, 1299); **10a** (Klein, C. L.; Conrad, J. M.; Morris, S. A. *Acta Crystallogr.* **1985**, *C41*, 1202); **10c** (Borowicz, P.; Herbich, J.; Kapturkiewicz, A.; Anulewicz-Ostrowska, R.; Nowacki, J.; Grampp, G. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4275). Bond lengths are in reasonable agreement with those calculated in the present work; however, the trends we observe in the calculated data are more difficult to detect due to the subtleties of the trends and the inevitably limited precision of the X-ray work. The crystallographic data also confirm the highly twisted nature of **8** and **10** systems suggested by the calculations, but we have chosen not to compare exact torsion angles because the X-ray values are subject to intermolecular packing effects not considered in the calculations.

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(49) (a) SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/. (b) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553. (c) Magdolen, P.; Meciarová, M.; Toma. *Tetrahedron* **2001**, *57*, 4781. (d) Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron* **1999**, *55*, 12829.

(50) Experimental ^{13}C NMR data (δ in $CDCl_3$) for the new compounds are as follows. Spectra were assigned with the assistance of gradient-decoupled HSQC and gradient-decoupled HMBC experiments. Full synthetic and characterizing data for these compounds will be published elsewhere. **9b**: 190.8 (CHO), 144.8 (phenylene C1), 143.3 (dithienopyrrole quat), 133.4 (phenylene C4), 131.6 (phenylene C3,5), 124.2 (dithienopyrrole CH), 121.8 (phenylene C2,6), 118.5 (dithienopyrrole quat), 112.3 (dithienopyrrole CH). **10b**: 190.6 (CHO), 150.4 (phenylene C1), 141.4 (phenothiazine quat), 132.6 (phenylene C4), 131.9 (phenylene C2,6), 130.7 (phenothiazine CH), 128.9 (phenylene C3,5), 127.5 (phenothiazine CH), 126.2 (phenothiazine CH), 125.6 (phenothiazine CH), 117.3 (phenothiazine CH). **11b**: 181.0 (CHO), 166.5 (thiophene N−C quat), 158.1 (anisyl C−O quat), 139.3 (anisyl C−N quat), 139.0 (thiophene C−CHO quat), 128.7 (thiophene CH adjacent to CHO), 127.4 (anisyl C2,6), 115.2 (anisyl C3,5), 109.4 (thiophene CH adjacent to N), 55.8 (Me). We also report the ^{13}C NMR spectrum of the known compound **7b** in $CDCl_3$ for the first time: 190.3 (CHO), 157.4 (anisyl C−O quat), 154.1, 138.9 (anisyl C−N quat), 131.5 (phenylene 3,5), 128.2 (anisyl CH), 127.9 (phenylene C4), 116.9 (phenylene 2,6), 115.2 (anisyl CH), 55.7 (Me).