The Azine Bridge as a Conjugation Stopper: An NMR Spectroscopic Study of Electron Delocalization in Acetophenone Azines†

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Dipole parallel-alignment of organic molecular crystals of azines has been achieved with a design that was based on the hypothesis that the azine bridge is a conjugation stopper. This hypothesis has now been tested in detail, and ^{1}H and ^{13}C NMR spectroscopic data of symmetric and unsymmetric acetophenone azines are presented in support of this design concept. Previous structural, ab initio, and electrochemical studies have shown that the azine bridge largely inhibits through-conjugation in molecules with the general structure DPhC(Me)═N−N═C(Me)PhA, where D is a donor group and A is an acceptor group. NMR spectroscopy is an excellent tool to probe the degree of conjugation through the azine bridge. The NMR results reported here for nine symmetrical and 18 unsymmetrical azines show in a compelling fashion that the hypothesis holds. Varying the donor group does not change the chemical shifts of the aromatic hydrogen and carbon atoms on the acceptor-substituted phenyl ring. Likewise, varying the acceptor group does not change the chemical shifts of the atoms in the donor-substituted phenyl ring.

Introduction

The design of highly polar materials is important for numerous optical and electrical properties. For instance, the two key requisites for a crystal to exhibit a nonlinear optical (NLO) response are a macroscopic dipole moment and a non-centrosymmetric structure.[1] Many organic compounds crystallize in non-centrosymmetric space groups[2] without realizing any NLO effects,[3,4] and thus, this is a relatively easy requirement to satisfy. The key to achieving an NLO response in crystals is the parallel alignment of the molecular dipole moments, and the preparation of crystals with large polarizations remains a challenge far beyond the quest for non-centrosymmetry.

The realization of macroscopic dipole moments for use in nonlinear optics[5] has largely been achieved in liquid crystals,[6] through poled polymers[7] and through the inclusion of NLO active chromophores into zeolites[8] and synthetic porous solids.[9] While interest in polar materials has been tightly linked to nonlinear optics, a polar environment is critical for many other optical and electrical properties, such as thermal conductivity,[10] ferroelectric[11] and ferroelastic responses,[12] and photorefractive applications.[13]

All of the approaches listed above for the design of polar order are far from optimal. The use of liquid crystals results in only a small excess of the molecules having their dipole moments aligned in a parallel fashion and thus the overall polarity is small. Poled polymers and inclusion compounds suffer from small chromophore densities and poled polymers also require the use of an electric field for poling. When the electric field is removed, the parallel alignment of the molecular dipole moments begins to deteriorate and eventually the polymeric system loses its NLO activity. The ultimate goal in the design of polar materials is to prepare molecular crystals which have their molecular dipole moments aligned in the same direction.

Recently, a high degree of dipole parallel-alignment has been achieved in organic molecular crystals consisting of conjugated donor−acceptor molecules.[14] Among the more highly dipole parallel-aligned organic molecular crystals are APDA,[15] DAD,[16] DMACB,[17] NPP,[18] and

† Stereochemistry and Stereoelectronics of Azines. 17. For part 16, see ref 22.

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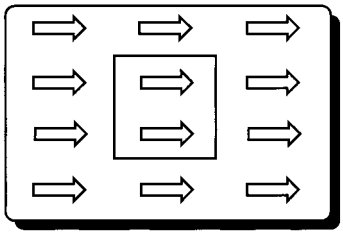
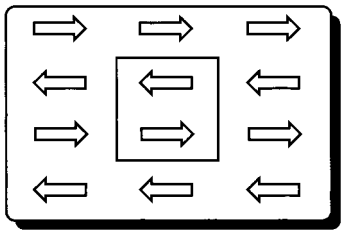
Chart 1

Parallel Dipole Alignment



(a)

Antiparallel Dipole Alignment

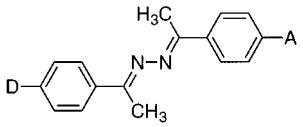


(b)

PNP.[19] Dipole parallel-alignment has also been achieved in the ionic organic crystals MC−PTS[20] and DAST.[21] These examples show that dipole parallel-alignment is feasible in organic molecular crystals, but since they were all prepared by different groups they do not reveal a systematic approach to the design of highly dipole parallel-aligned organic crystals. Thus, we initiated a program aimed at preparing and understanding the crystal packing of dipolar conjugated molecules with the impetus of systematically preparing dipole parallel-aligned molecular organic crystals.

The design of dipole parallel-aligned molecular organic crystals is a difficult proposal, and Chart 1 illustrates the primary complication. Chart 1a depicts our goal, the alignment of dipole moments in a crystal lattice. Chart 1b shows what most often occurs when polar molecules aggregate in the solid phase: the molecules align such that their molecular dipole moments cancel and the dipole moment of the crystal is zero. We have developed two concepts in our approach to design molecules that crystallize in the general motif displayed by Chart 1a. Our first strategy involves the use of polar chromophores that contain fragments that can act as lateral synthons.[22] Molecular fragments capable of binding with certain other atoms or functional groups with high selectivity and high affinity are referred to as synthons.[23] Thus, a lateral synthon is an interaction that occurs between molecules within the same two-dimensional layer. We have employed the arene−arene interaction as the key lateral synthon, and the energy gained from this interaction can aid in overcoming the electrostatic repulsion due to dipole parallel alignment. The second strategy we have used in our design is ground-state dipole moment minimization via the incorporation of an azine bridge (>C═N−N═C<) between donor−acceptor-substituted π-systems. The placement of the azine bridge essentially puts two acceptor groups between the donor−acceptor substituents. This results in one-half of the chromophore being a classical donor−acceptor π-system while the other half is an acceptor−acceptor π-system that does not contribute to the molecular dipole moment. It is for this reason that we hypothesize that the azine bridge decreases the molecular dipole moment. Dipole moment minimization is desirable because simple logic dictates that the larger the molecular dipole moment, the more difficult it is to achieve dipole parallel-alignment.[24]

Chart 2



The two design concepts described above led us to investigate acetophenone azines with the general formula DPhC(Me)═N−N═C(Me)PhA (D = donor, A = acceptor, see Chart 2) as candidates for dipole parallel-alignment. We have studied the crystal packing and electronic properties of symmetric (D = A)[25] and unsymmetric (D ≠ A)[26] acetophenone azines. Our investigations have resulted in the preparation of six unsymmetrical azines that exhibit a high degree of dipole parallel-alignment in the solid phase. The molecular structures of these six azines are as follows: D = OCH_3; A = Cl,[26b] Br[26g] and I[26a] and D = OPh; A = Cl, Br and I (Chart 2).[27]

We reported X-ray crystallographic[26a−d,g] and ab initio quantum mechanical[26e] results in support of our hypothesis that the azine bridge acts to impede through-conjugation between the two donor−acceptor-substituted phenyl rings. Several electrochemical studies support this notion. Over 40 years ago, Lund[28] studied the electrochemical reductions of benzaldazine and of the benzylhydrazone of benzaldehyde and found essentially the same reduction potential for the C═N reductions of the

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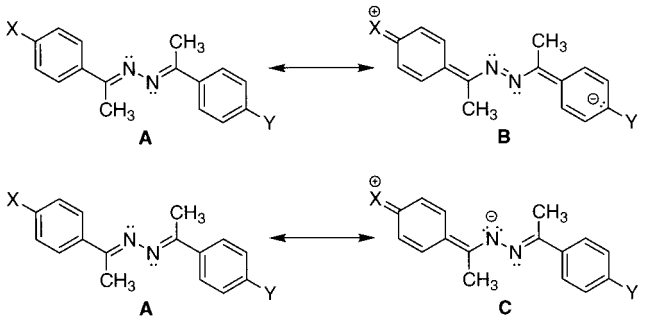
azine and the hydrazone. Recently, Ludvik, Zuman, et al.[29] studied the electrochemical reduction of metamitron, a triazine that contains an azine group, and found that there was hardly any electronic interaction between the two imine bonds. In 2000, Zuman and Ludvik[30] examined a broader series of triazines and also of acyclic azines, and they concluded that delocalization in both cyclic and acyclic molecules is either minimal or absent. Most recently, the electrochemical studies by Sauro and Workentin[31] showed this to be true more generally for a series of acetophenone azines. Two assumptions are implicit in the deductions made in these electrochemical studies. First, it is assumed that the only difference between the C=N bonds in a hydrazone and an azine would be the occurrence of delocalization in the azine. However, one needs to recognize that differences in the σ-system occur as well depending on the sp^2 (azine) or sp^3 (hydrazone) hybridization of the N atom attached to the imine-N and, in fact, the authors of the above-described electrochemical studies do point to the potential role of inductive effects. Second, the electrochemical studies reflect both the properties of the neutral azine (or hydrazone) *and* of the respective reduction product. The reduction product is a radical anion and substituent effects on these high-energy intermediates might be large. Here we present ^{1}H and ^{13}C NMR spectroscopic data to further support the idea of the azine bridge functioning as a conjugation stopper. The NMR measurements depend only on the properties of the neutral azines and any conclusions derived from the NMR data do not require assumptions as to the electronic properties of any other class of compounds. The general structure of the azines that we will discuss in this article is shown in Chart 2. The donor substituents are D = OCH_3, NH_2 and OPh and in each case they are coupled with the acceptors A = F, Cl, Br, I, CN and NO_2. For comparison, we also include the NMR data for the respective symmetric azines where D = A.

Experimental Methods

The syntheses of the 18 unsymmetrical azines and nine symmetrical azines have been reported elsewhere for many of the molecules.[25a,b,26a−d,g] Generally, the donor-substituted acetophenone is reacted with hydrazine hydrate to yield the respective hydrazone. The hydrazone is then reacted with the acceptor-substituted acetophenone to give the desired unsymmetrical product. The symmetric acetophenone azines were prepared in the same manner except in the last step the hydrazone is reacted with a like-substituted acetophenone. The products were purified via column chromatography. The ^{1}H and ^{13}C NMR data were measured in deuterated chloroform with an 250 MHz NMR instrument (operating frequencies for ^{1}H and ^{13}C of 250.131 532 1 and 62.902 369 4 MHz, respectively) and a 300 MHz (operating frequencies for ^{1}H and ^{13}C of 300.131 770 8 and 75.476 916 4 MHz, respectively) NMR spectrometer.

We assigned the chemical shifts of the aromatic hydrogen and carbon atoms of the symmetric acetophenone azines by comparing them to the empirical values obtained via the chemical shift constants of para-substituted arenes.[32] A chemical shift constant for the azine functionality has not yet been determined and therefore we used the chemical shift constant for the acetyl group as an approximation. We then used the chemical shifts of the aromatic H and C atoms of the symmetric azines to assign the shifts of the unsymmetrical molecules. This method of assigning the chemical shifts of the aromatic H and C atoms in the unsymmetrical azines assumes that the azine bridge acts as a conjugation stopper and the assumption is justified by the structural,[26a−d,g] ab initio[26e] and electrochemical[28−31] results previously presented. Chemical shift data are presented in four tables in the Supporting Information.

Scheme 1



Results and Discussion

Electron Delocalization. The basic query that we address in this paper is if through-conjugation traverses the entire length of the unsymmetrical acetophenone azines, as is common for donor−acceptor conjugated molecules and is described by the neutral resonance form **A** and a significant contribution by the resonance form **B** as well (Scheme 1). The **C** resonance form exemplifies one of the resonance forms for the conjugation of D with the benzene ring and if the azine bridge behaved as a conjugation stopper then there is no possibility to delocalize negative charge accumulated on the N-atom into the other half of the molecule. We can discern between these modes of electron delocalization by comparing the aromatic ^{1}H and ^{13}C NMR chemical shifts for the symmetric acetophenone azines with the chemical shifts of the unsymmetrical azines. If the resonance form **B** does contribute significantly, then varying the donor substituent should change the aromatic ^{1}H and ^{13}C NMR chemical shifts on the acceptor-substituted arene ring. Likewise, varying the acceptor group should change the ^{1}H and ^{13}C NMR chemical shifts on the donor-substituted ring. If the azine bridge is indeed inhibiting through-conjugation, then varying the donor substituent should not affect the aromatic ^{1}H and ^{13}C NMR chemical shifts on the acceptor-substituted phenyl ring. Similarly, varying the acceptor group should not change the ^{1}H and ^{13}C NMR chemical shifts on the donor-substituted ring. If through-conjugation in acetophenone azines is of marginal importance only, then we would be able to assign the ^{1}H and ^{13}C aromatic chemical shifts of the unsymmetrical azines based on the chemical shifts of the respective symmetric molecules. For instance, in the unsymmetrical azine where D = OCH_3 and A = Br, we would expect the ^{1}H and ^{13}C aromatic chemical shifts of the methoxy-substituted phenyl ring to be the same as the chemical shifts in the symmetric azine where D = A = OCH_3.

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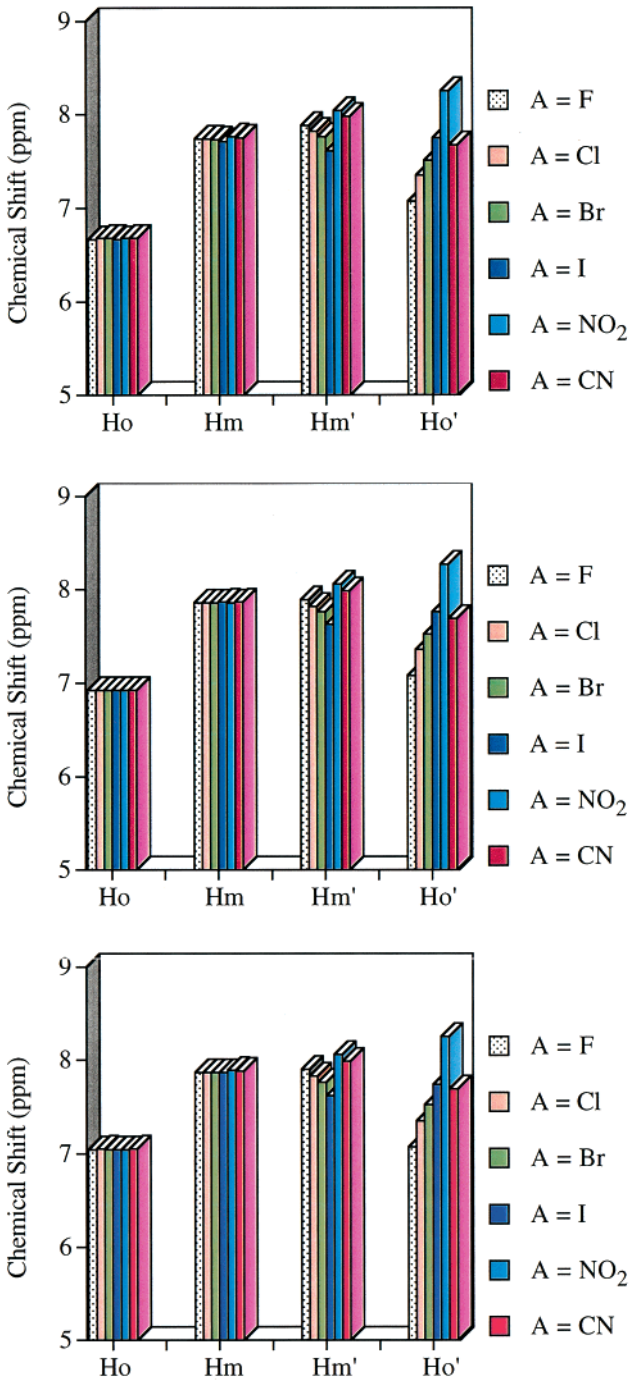

Figure 1. Bar graphs representing the chemical shifts of the aromatic hydrogen atoms for the amino- (**10**−**15**, top), the methoxy- (**16**−**21**, middle), and the phenoxy-substituted unsymmetrical acetophenone azines (**22**−**27**, bottom).

The ^{1}H and ^{13}C aromatic chemical shifts offer a good probe for the extent of through-conjugation in molecules with the general structure shown in Chart 2 because several of the NMR shielding terms are sensitive to the flow of electrons.[33] The diamagnetic shielding term is directly related to atomic charge, and in turn, the charges on the aromatic hydrogen and carbon atoms will be sensitive to conjugative effects. Changes in electron density due to through-conjugation will also effect the

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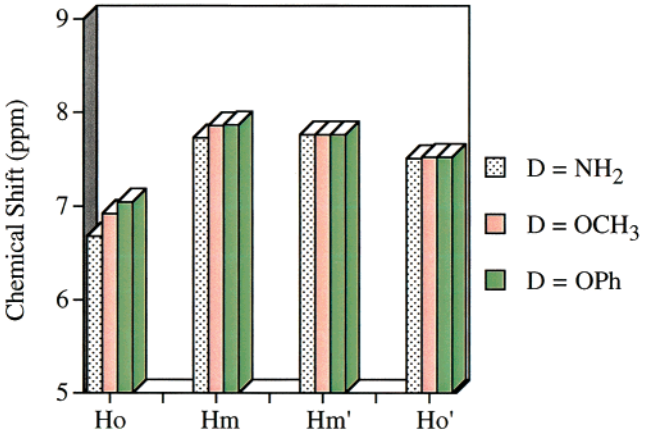
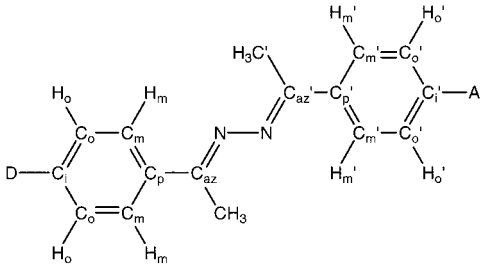


Figure 2. Bar graph representing the chemical shifts of the aromatic hydrogen atoms for the bromo-substituted unsymmetrical acetophenone azines **12**, **18**, and **24**.

Chart 3



paramagnetic shielding term, and this will be manifest in the signals of the aromatic carbon atoms.

^{1}H NMR Spectroscopic Results. The empirical and experimental ^{1}H aromatic chemical shifts for the 4-substituted symmetrical fluoro- (**1**), chloro- (**2**), bromo- (**3**), iodo- (**4**), nitro- (**5**), cyano- (**6**), amino- (**7**), methoxy- (**8**), and phenoxyacetophenone azine (**9**) are collected in Table 1 in the Supporting Information. The empirically determined chemical shifts are exceptionally accurate in predicting the chemical shifts of the symmetric acetophenone azine. Furthermore, the measured data also justifies our use of the acetyl group chemical shift constant as an approximation for the chemical shift constant for the azine bridge. Chart 3 shows the H atoms that we focus on in this study. For the symmetric azines reported in Table 1, D = A, $H_o = H_o'$ and $H_m = H_m'$.

The ^{1}H aromatic chemical shift data for the unsymmetrical acetophenone azines are collected in Table 2 in the Supporting Information. The molecules with D = NH_2 and A = F, Cl, Br, I, NO_2, and CN are numbered **10**−**15**, the azines with D = OCH_3 and A = F, Cl, Br, I, NO_2, and CN are numbered **16**−**21**, and those with D = OPh and A = F, Cl, Br, I, NO_2, and CN are numbered **22**−**27**. The H_o, H_o', H_m, and H_m' hydrogen atoms refer to the H atoms depicted in Chart 3. Figure 1 shows in a compelling fashion that the aromatic hydrogen atoms on the donor-substituted phenyl ring are not affected by a change of the acceptor group. For the amino-substituted unsymmetrical azines, the chemical shift of the H atoms ortho to the donor substituent vary by only 0.01 ppm and the chemical shift of the meta hydrogen atoms vary by just 0.05 ppm (Figure 1, top). For the methoxy-substituted unsymmetrical azines, the chemical shifts of the ortho and meta hydrogen atoms vary by 0.02 and 0.03 ppm (Figure 1, center) and for the phenoxy-substituted azines

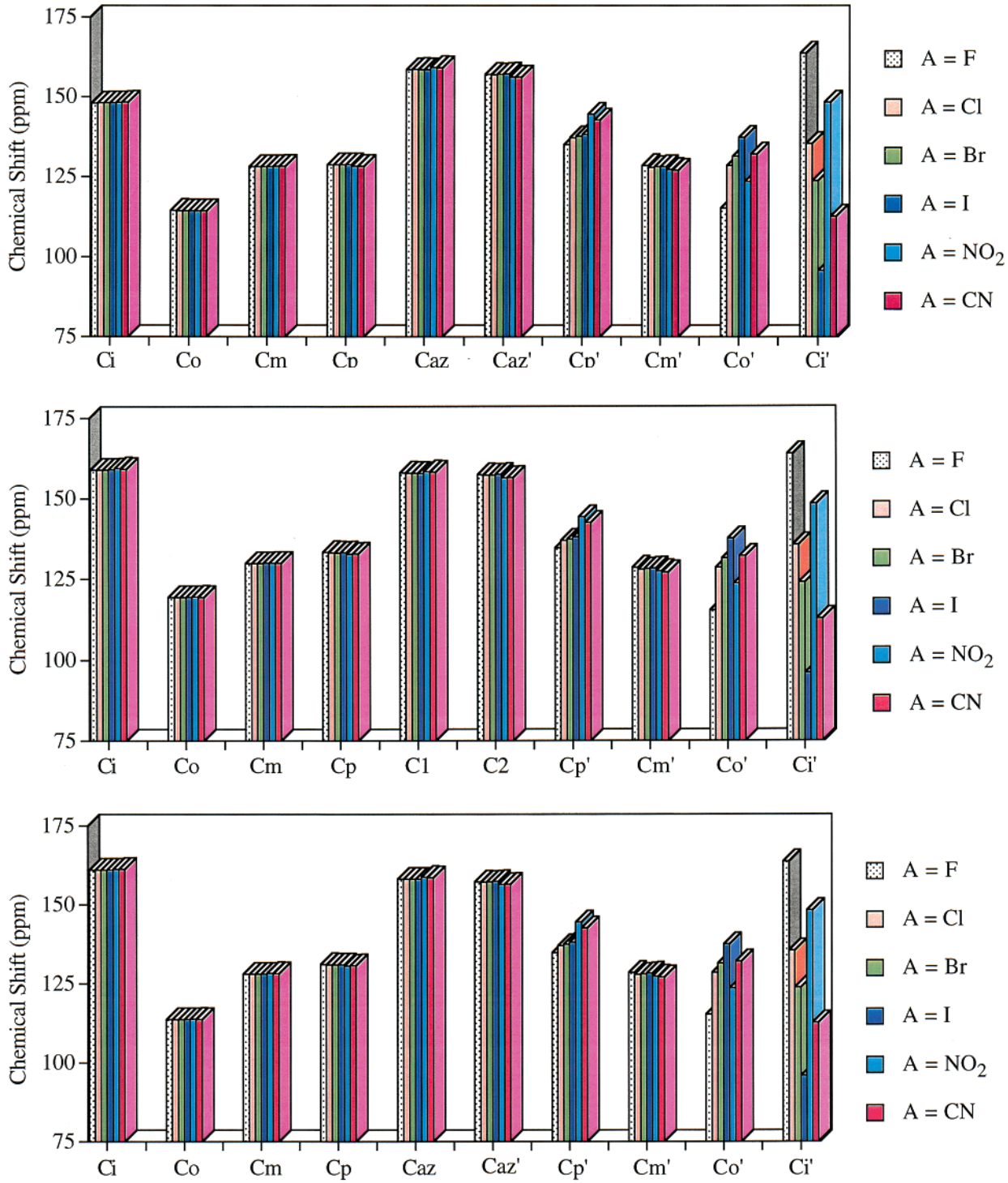


Figure 3. Bar graphs representing the chemical shifts of the aromatic carbon atoms for the amino- (**10**−**15**, top), the methoxy- (**16**−**21**, middle), and the phenoxy-substituted unsymmetrical acetophenone azines (**22**−**27**, bottom).

the variation is 0.01 and 0.03 ppm (Figure 1, bottom). Moreover, the aromatic ^{1}H chemical shifts of the symmetric amino-, methoxy-, and phenoxy-substituted azines are essentially the same as the ^{1}H chemical shifts in the donor-substituted halves of the unsymmetrical acetophenone azines presented in Table 2 and Figure 1. The ^{1}H chemical shifts of the amino, methoxy and phenoxy substituents are also largely unaffected by the nature of the donor group. The chemical shifts of the amino hydrogen atoms in **10**−**15** are 3.86 ± 0.03 ppm and the ^{1}H shifts of the methoxy hydrogen atoms in **16**−**21** are 3.84 ± 0.01 ppm. The hydrogen atom chemical shifts in the phenoxy substituents are 7.01 ± 0.01 ppm for the H atoms ortho to the oxygen atom, 7.35 ± 0.01 ppm for the meta hydrogen atoms, and 7.14 ± 0.02 ppm for the para hydrogen atoms.

The measurements also demonstrate that the chemical shifts of the aromatic H atoms on the acceptor-substituted phenyl ring are unaffected by variations in the donor group. The impervious nature of the acceptor-

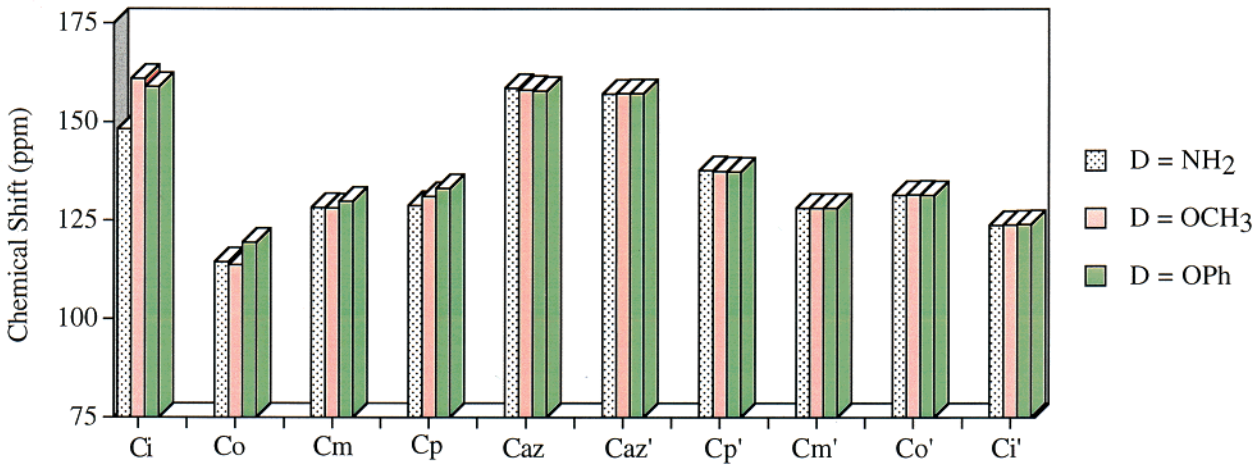


Figure 4. Bar graph representing the chemical shifts of the aromatic carbon atoms for the bromo-substituted unsymmetrical acetophenone azines **12**, **18**, and **24**.

substituted phenyl ring to the donor substituent is illustrated in Figure 2 where the acceptor group is bromine. The chemical shifts of the H atoms ortho to the bromine atom are 7.51 ± 0.01 ppm when the donor group is varied (Table 2) and the chemical shifts of the meta hydrogen atoms remain constant at 7.76 ppm regardless of the donor substituent. The same trend holds for the other acceptor groups.

^{13}C NMR Spectroscopic Results. The empirical and experimental ^{13}C aromatic chemical shifts for molecules **1**−**9** are collected in Table 3 in the Supporting Information. As was the case for the ^{1}H NMR chemical shifts, the empirically determined ^{13}C chemical shifts are very accurate in predicting the chemical shifts of the symmetric acetophenone azine. The acetyl group chemical shift constant again serves as a good approximation for the chemical shift constant of the azine bridge. Chart 3 shows the carbon atoms we focus on in this study. For the symmetric azines reported in Table 3, D = A, $C_i = C_i'$, $C_o = C_o'$, $C_m = C_m'$, and $C_p = C_p'$. The main advantage of the ^{13}C NMR data over ^{1}H data is that it allows us to probe the effects of conjugation further along the molecular framework. The ^{1}H data allowed us to probe only to the positions ortho and meta to the donors and acceptors while the ^{13}C data reveals the effects of conjugation at all four unique aromatic positions as well as in the azine carbon atoms (C_{az} and C_{az}').

The measured ^{13}C chemical shifts for acetophenone azines **10**−**27** are collected in Table 4 in the Supporting Information. The C_i, C_i', C_o, C_o', C_m, C_m', C_p, and C_p' carbon atoms refer to the C atoms depicted in Chart 3. Figure 3 demonstrates graphically that the aromatic carbon atoms on the donor-substituted phenyl ring are not affected by changing the acceptor group. For the amino-substituted unsymmetrical azines, the chemical shift of the carbon atom ipso to the donor substituent varies by 0.04 ppm, the ortho C atoms vary by just 0.01 ppm, the meta C atoms vary by 0.02 ppm, and the para C atom varies by 0.05 ppm (Figure 3, top). Similar small variations are seen for the methoxy- and phenoxy-substituted phenyl rings (Figure 3 middle and bottom graphs). The aromatic ^{13}C chemical shifts for the donor-substituted phenyl rings in azines **10**−**27** are essentially the same as the shifts in the respective symmetric azine **1**−**9** (Table 3). The ^{13}C chemical shifts of the methoxy and phenoxy substituents are also largely unaffected by the nature of the donor group. The ^{13}C chemical shifts of the methoxy carbon atom in azines **16**−**21** range from 55.3 to 55.4 ppm. The ^{13}C chemical shifts of the carbon atoms in the phenoxy-substituted azines range from 156.4 to 156.6 ppm for the carbon atom ipso to the oxygen atom, from 118 to 118.1 ppm for C_{ortho}, from 128.2 to 128.4 ppm for the C_{meta}, and from 123.7 to 123.9 ppm for C_{para}.

Our measured data also demonstrates that the aromatic ^{13}C chemical shifts of the donor-substituted phenyl ring are unaffected by variations in the acceptor group, and this is illustrated in Figure 4 for the set of molecules with A = Br. The chemical shifts of the carbon atoms on the bromo-substituted phenyl ring vary by less than 0.4 ppm for the three different donor groups. The same trend holds for the other acceptor groups. The ^{13}C chemical shift of the cyano carbon atom in molecules **6**, **15**, **21**, and **27** can also serve as a probe of how the acceptor-substituted phenyl ring is unaffected by variations in the donor group. The ^{13}C chemical shift of the cyano carbon atom in these four molecules only varies by 0.2 ppm, from 118.7 to 118.9 ppm.

The ^{13}C NMR data for the C atom of the azine unit does not change significantly upon varying either the donor- or the acceptor-group. For instance, for molecules **10**−**15**, the ^{13}C chemical shifts for the azine C atom on the donor-substituted phenyl ring range from 158.5 to 159.2 ppm and the ^{13}C chemical shifts for the azine C atom on the acceptor-substituted phenyl are between 156.3 and 157.4. This lack of substituent effect on the C atom of the azine unit may suggest a prevalence of an inductive effect rather than a conjugative effect. Regardless, the results clearly show the lack of through conjugation in acetophenone azines.

Conclusions

Our group has successfully prepared six near-perfectly dipole parallel-aligned molecular organic crystals. Two key design concepts were employed in our approach to these six materials. First, we utilized arene−arene interactions as lateral synthons in order to generate the attraction required to overcome dipole parallel-alignment. Second, we used the azine bridge as a means to decrease the molecular dipole moment because dipole moment minimization increases the possibility of dipole parallel-alignment. Crystallographic, electrochemical and ab ini-

tio results have suggested that the azine bridge acts to inhibit the flow of electrons in donor−acceptor acetophenone azines. In this article we presented ^{1}H and ^{13}C NMR spectroscopic data to further support the theory that the azine bridge acts as a conjugation stopper. The chemical shifts of the aromatic hydrogen atoms of the donor-substituted aromatic ring are unaffected by the nature of the acceptor substituent. Likewise, the ^{1}H chemical shifts of the acceptor-substituted ring remain constant upon varying the donor group. Since the ^{1}H chemical shifts only allow to probe the ortho and meta positions on the aromatic rings, we also measured the ^{13}C chemical shifts as a means of studying the effects of conjugation further along the molecular skeleton. The ^{13}C chemical shifts exhibit the same trends as the ^{1}H shifts; the nature of the acceptor group has no effect on the ^{13}C chemical shifts of the donor-substituted phenyl ring and vice versa. The NMR chemical shift data reported in the present study fully corroborates that the azine bridge does act as a conjugation stopper.

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Supporting Information Available: Four tables containing the empirical and experimental ^{1}H and ^{13}C chemical shifts for symmetrical acetophenone azines **1**−**9** and ^{1}H and ^{13}C NMR chemical shifts for the unsymmetric acetophenone azines **10**−**27**. This material is available free of charge via the Internet at http://pubs.acs.org.

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