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# Asymmetrization Effects on Structures and Populations of the Ground State of Dipolar Donor–Acceptor-Substituted Molecular Organic NLO Materials

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**ABSTRACT:** Asymmetric donor–acceptor-substituted  $\pi$ -conjugated systems with low dipole moments and structural components that favor parallel alignment of neighboring molecules are potential molecular organic materials with nonlinear optical properties for which near perfect dipole parallel alignment is possible. The asymmetrical 4-methoxysubstituted acetophenone azines with the substituents fluorine (1), chlorine (2), bromine (3), cyano (4), and nitro (5) in the 4'-position have been studied in this context, and for 2 and 3 the dipole parallel alignment has indeed been accomplished in crystals of the pure material. In the present study, the effects of asymmetrization on the structure and the electronic structures of the ground states of 1–5 have been explored at the RHF/6-31G\* level. The properties of the optimized structures of the azines 1–5, a comparative analysis of asymmetrical and symmetrical azines, and natural population analyses, all show no significant evidence for conjugation over the azine bridge. The concept of azine spacers as “conjugation stoppers” is useful and the dipole moments of asymmetrical azines are relatively small. The analysis suggests that the charge transfer between the donor and acceptor contributes to the dipole moment much less than is generally assumed. © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 1130–1140, 1998

Dedicated to Prof. N. L. Allinger

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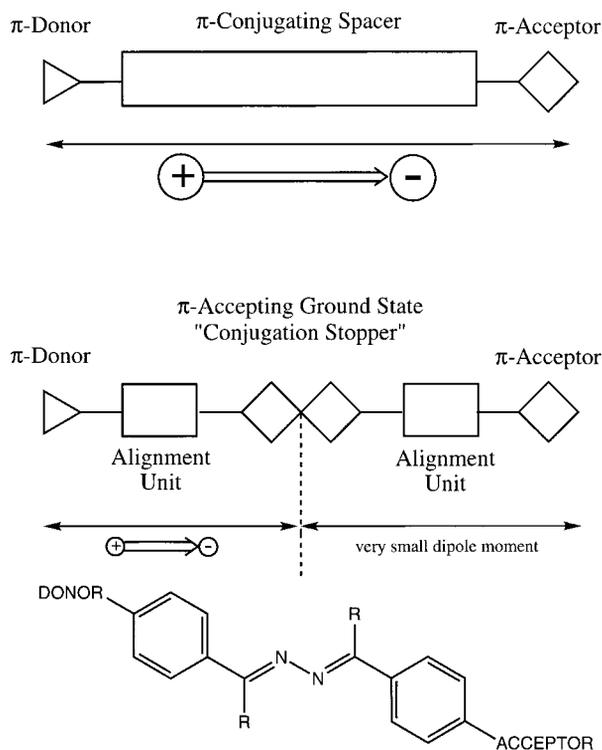
**Keywords:** asymmetrization effects; electron donor–acceptor; materials for nonlinear optics; population analysis; dipole alignment; structural effects of conjugation

## Introduction

For materials to show nonlinear optical effects<sup>1–6</sup> in the solid state, it is essential that the molecules are packed in such a way as to produce a nonzero macroscopic electrical dipole moment. This requirement is difficult to meet because electrostatic forces tend to align polar molecules such that molecular dipoles cancel. Only small overall dipole moments were realized in noncentrosymmetric crystals of NLO materials where the cancellation of nearly antiparallel-aligned NLO chromophores is incomplete.<sup>7</sup> Current developments of organic NLO materials focus almost exclusively on achieving electric-field-aligned NLO chromophores in polymer matrices<sup>8</sup> and to a lesser degree on inclusion systems.<sup>9</sup> These approaches all suffer from low dipole densities and incomplete alignment and these disadvantages will become magnified because the device size needs to be reduced in practical applications in the near future.

Numerical simulations of the electrostatic interactions of dipole parallel-aligned lattices clearly show that such lattices can be formed exothermically.<sup>10</sup> The lattice energies computed for antiparallel-aligned three-dimensional-point dipole distributions of the same dipoles at similar distances are, of course, more exothermic than for the parallel-aligned lattices. To overcome the dipole alignment problem one thus needs to design molecules with NLO chromophores that clearly do not favor nonparallel alignment. If this condition is met, so that the dipole antiparallel-aligned and the dipole parallel-aligned lattice can both exist as (local) minima, then one can think of ways to make the dipole parallel-aligned lattice the thermodynamically preferred phase if the molecules are designed such that they allow for additional nondipole interactions. In our design, the NLO chromophores are based on donor–acceptor-substituted conjugated systems and they incorporate several novel design ideas (Scheme 1). In general, the donor and acceptor groups are selected to optimize intra- and

intermolecular interactions.<sup>11</sup> Central to our chromophore design is the minimization of the ground state dipole moment in a way that does not impede strong charge transfer upon electronic excitation. Relatively small ground state dipole moments are required to make the dipole parallel- and antiparallel-aligned systems competitive. This design goal is accomplished by placing two polar acceptor groups with opposite orientations in the center of the molecule. In a way, this design replaces one dipole with a large distance between the donor and the acceptor with one dipole with a small distance between the donor and the proximate acceptor in the center of the molecule. With the commonly made assumption that the dipole moment of the molecule reflects the charge transfer between the donor and the acceptor due to conjugative interaction in the ground state, this design would effectively reduce the dipole as the central acceptors act as an efficient “conjugation



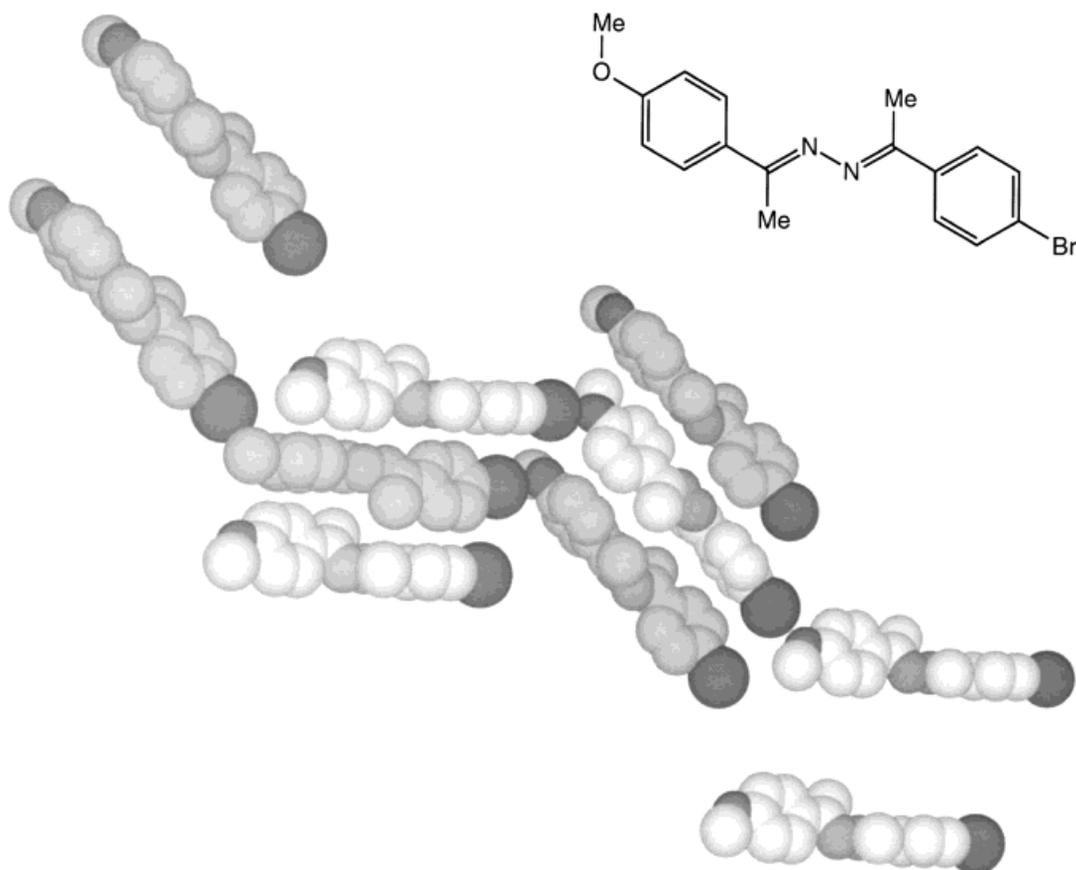
**SCHEME 1.**

stopper." The remainder of the molecule becomes quadrupolar and contributes little to the overall dipole moment. Another important design feature relates to the inclusion of aromatic systems. Arene-arene interactions<sup>12</sup> can contribute significantly to lattice energies, even at relatively long distances, and we employ these attractive interactions to compensate for electrostatic repulsions associated with the parallel-aligned molecular dipoles.

Asymmetrical acetophenone azines (Fig. 1) present an ideal realization of this concept. Azines,<sup>13</sup> 2,3-diaza derivatives of butadiene, formally are products of condensation between a molecule of hydrazine and two carbonyl compounds. Azines are referred to as symmetrical or asymmetrical, respectively, if the two carbonyl compounds from which the azine is derived are the same or different. Asymmetrical azines with acceptor and donor groups in the *para* positions of the benzene rings

on opposing ends of the hyperpolarizable  $\pi$ -electron system may be excellent candidates for NLO materials and preliminary experimental and theoretical data indeed show this to be the case.<sup>14</sup> Azo compounds are closely related to azines and they have demonstrated remarkable NLO properties. Indeed, with the azine, 4-methoxy-4'-bromoacetophenone azine (Fig. 1), we have achieved, for the first time, near perfect parallel alignment of NLO active molecules in pure crystals to produce NLO chromophore densities and degrees of alignment that are unprecedented.<sup>15,16</sup>

In this context, we have studied the stereochemistry and stereoelectronics of symmetrical and asymmetrical acetophenone azines systematically for some time. The phenylsubstituted azines play an especially important role in azine chemistry and issues of conjugation in acetophenones are particularly pertinent. We explored N-N conformational and configurational preferences and Ph-C



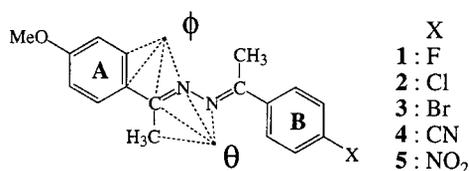
**FIGURE 1.** Packing for the 4-bromo-4'-methoxyacetophenone azine.

rotational barriers in a study of the stereochemistry of benzoylformate azines in the solid state, in solution, and in the gas phase<sup>17</sup>; we communicated a solid state study of symmetrical *para*-halogen-substituted acetophenone azines<sup>18</sup>; discussed implications of the polymorphism of *para*-methyl acetophenone azine<sup>19</sup>; and presented a comprehensive analysis of the solid state structures of 14 symmetrical (*E, E*)-configured *para*-disubstituted acetophenone azines.<sup>20</sup> Our studies to date have shown no evidence for strong conjugation effects in the symmetrical azines found in the solid state, in solution, and in the gas phase. We have shown that these azines prefer the N—N *gauche* conformation and that the phenyl rings tend to be twisted out of the best plane of the azine functional group, and these features are not consistent with the notion of conjugative interactions. More recently, we began to report on our studies of asymmetrical azines. A series of 4-methoxy-substituted asymmetrical acetophenone azines was synthesized with the following substituents in the 4' position: F (1), Cl (2), Br (3), CN (4), and NO<sub>2</sub> (5).<sup>14</sup> The crystal structures of azines 3–5 were determined and have been examined.<sup>21, 22</sup> In the meantime, we have also succeeded in growing crystals of the (Cl, MeO)—2 azine and its crystal structure contains a very similar motif such as in the case of the (Br, MeO)—3 azine.<sup>23</sup> Even with strong push–pull substitution, the asymmetrical acetophenone azines were found to still prefer the N—N *gauche* conformation and to exhibit phenyl twists in the solid state. These features turned out to be crucial for the formation of pairs of dipole parallel-aligned azine with intermolecular T-shaped arene–arene contacts in the crystals, and the nonplanarity was found not to have disadvantageous effects on hyperpolarizabilities. In the present study, we begin to examine the design ideas in detail and report the results of a study on the effects of asymmetrization on the geometries and electronic structures of the acetophenone azines 1–5. It is hoped that a better understanding of the relationships<sup>5</sup>

between the geometry and the electronic structure of the NLO material, on one hand, and its NLO activity and crystal structure, on the other hand, will allow for gradual refinement of successful design ideas and perhaps even lead to the discovery of new, desirable features.

## Theory and Computations

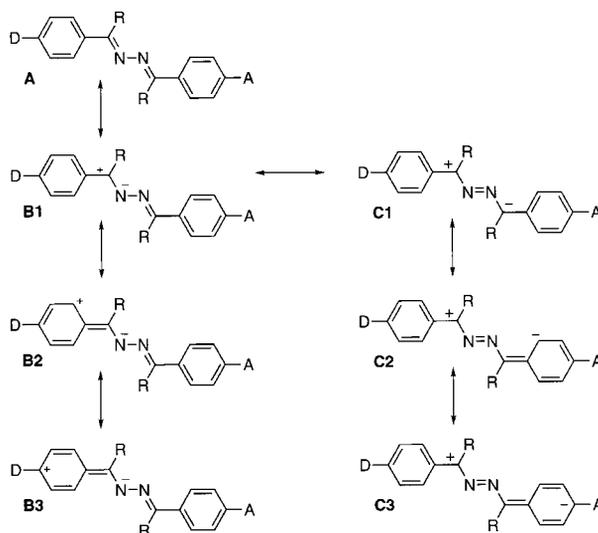
*Ab initio* calculations<sup>24</sup> were carried out with GAUSSIAN-94<sup>25</sup> and earlier versions on IBM/RS-6000 systems and Silicon Graphics Indigo and PowerChallenge L computers. Several structures were optimized for each of the azines and their symmetries are given in the tables. We first optimized the structure without any symmetry constraints and the resulting structures are referred to as the **a**-structures. To examine the C=N—N=C conformation and phenyl ring twists, we optimized two structures in C<sub>1</sub> symmetry with either the single constraint,  $\tau = 180^\circ$  (**b**-structures), or the more restrictive constraint to C<sub>s</sub> symmetry (**c**-structures), respectively. Stationary structures were characterized by analytical calculation of the vibrational frequencies to confirm that a stationary structure had been reached and to determine its character via the number of imaginary frequencies. Natural populations were determined to probe the electronic structures and the natural bond orbital (NBO) analysis employed the NBO module<sup>26</sup> embedded in the GAUSSIAN program. Geometry optimizations, frequency calculations and population analyses all were carried out at the restricted Hartree–Fock (RHF) level with the 6-31G\* basis set. The all-electron double- $\xi$  basis set, suggested by Huzinaga<sup>27</sup> was used for bromine. This basis set is of the type (4333/433/4); that is, the four s-type basis functions are contractions of four (1s) or three (2s–4s) primitives, the three p-type basis functions are contractions of four (2p) or three (3p, 4p) primitives, and the 3d basis functions are constructed from four primitives. This basis set was improved in that the outermost basis function of each type was split such that outermost primitives became basis functions by themselves. To complete the Br basis set, a set of polarization functions was added (exponent 0.389) and this augmentation was indicated by the addition of "1\*" to the basis set descriptor and the resulting basis set is denoted as (43321/4321/311\*).<sup>27b</sup>



## Results and Discussion

### RESONANCE STRUCTURES AND AZINE GEOMETRIES

Basic notions of conjugation would suggest planar structures for the acetophenone azines, and indeed conjugation arguments have routinely been used in discussions of azine structure and reactivity. The  $C_{2h}$  symmetry for the parent formaldiazine has been well established, but it is becoming clear that the situation is far more complicated for acetophenone azines. Expected effects on geometries as the result of contributions from various resonance forms for donor-acceptor systems of the type  $D_{para}-Ph-RC=N-N=CR-Ph-A_{para}$  can be deduced from Scheme 2.<sup>21</sup> On the donor side, significant contributions from **B** will result in longer C=N bonds, shorter  $C_{ipso}-C_{azine}$  bonds, and shorter D-C bonds. On the acceptor side, significant contributions from **C** will result in shorter N-N bonds, longer C=N bonds, shorter  $C_{ipso}-C_{azine}$  bonds, and shorter C-A bonds. Shorter N-N bonds and N-N *trans* conformations are expected if significant negative charge dispersal occurs. In contrast, significant contributions by the **B** forms would lead to an N-N *gauche* preference due to electron-electron repulsion. Finally, any significant conjugative interaction of the X substituent should favor coplanarity of the phenyl ring with the  $-CR=N-$  group. In



**SCHEME 2.**

studies of conjugation based on structural data, comparative analyses are required for series of closely related molecules that allow for the study of changes of structural parameters. Thus, we studied the symmetrical azines first to obtain the best possible reference. We prepared all of the necessary compounds, grew single crystals, and determined their structures by x-ray crystallography. Comparisons of selected bond lengths and torsion angles of 2-5 to the symmetrical *para*-disubstituted acetophenone azines with MeO, Cl, Br,

**TABLE I.**  
Comparison of X-Ray Structural Parameters of Symmetrical versus Asymmetrical Acetophenone Azines.

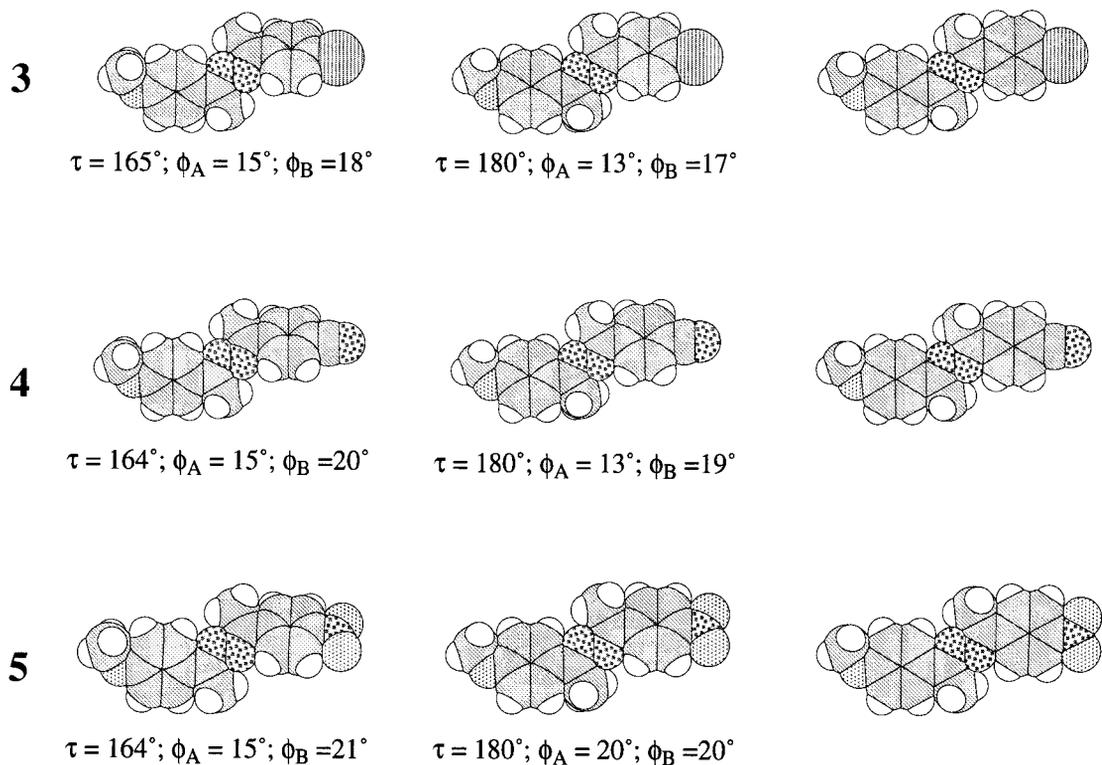
	Asymmetrical, <sup>a-c</sup> MeO—X						Symmetrical, <sup>d</sup> X—X				
	2 X = Cl	3A X = Br	3B X = Br	av(AB) X = Br	4 X = CN	5 X = NO <sub>2</sub>	MeO	Cl	Br	CN	NO <sub>2</sub>
X—C	1.737	1.916	1.894	1.905	1.438	1.462	1.364	1.742	1.904	1.435	1.456
Y—C	1.365	1.402	1.374	1.388	1.367	1.370		1.743	1.891		1.467
N—N	1.395	1.396	1.375	1.386	1.390	1.396	1.409	1.398	1.383	1.397	1.398
N=C <sub>A</sub>	1.288	1.253	1.314	1.284	1.277	1.293	1.281	1.288	1.264	1.277	1.280
N=C <sub>B</sub>	1.284	1.295	1.282	1.289	1.278	1.273		1.282	1.269		1.273
C <sub>ipso</sub> —C <sub>A</sub>	1.479	1.500	1.445	1.473	1.485	1.495	1.479	1.476	1.478	1.475	1.491
C <sub>ipso</sub> —C <sub>B</sub>	1.493	1.484	1.485	1.485	1.478	1.476		1.491	1.477		1.482
τ	134.7	137.5	136.1	136.8	117.9	134.1	180.0	134.7	124.6	180.0	152.0
φ <sub>A</sub>	14.9	13.5	3.1	8.3	14.0	1.4	10.7	30.3	27.2	0.5	1.2
φ <sub>B</sub>	4.0	8.9	17.9	13.4	16.3	5.2		30.5	20.9		14.0

<sup>a</sup>Y = MeO. **A** and **B** refer to the fragments with X and Y, respectively.

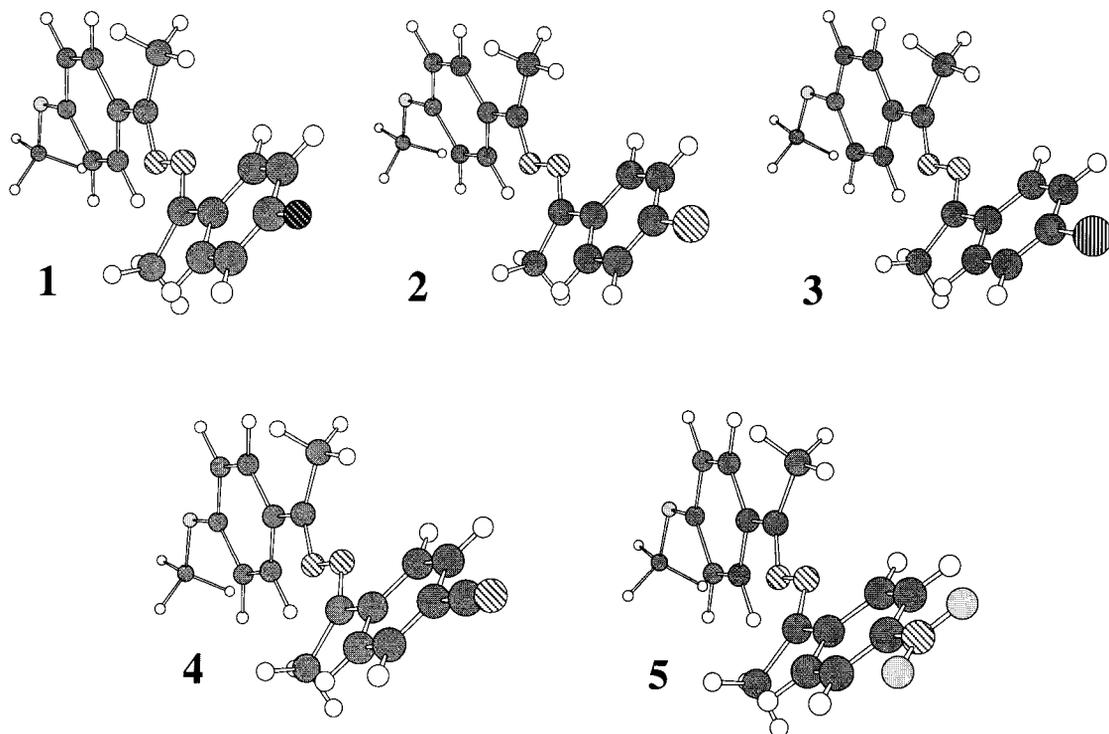
<sup>b</sup>Data for the asymmetrical azines are taken from ref. 21.

<sup>c</sup>Data refer to the nondisordered symmetry-independent molecule in the room temperature x-ray structure of **2** (ref. 23).

<sup>d</sup>Data for the symmetrical azines are taken from ref. 20.



**FIGURE 2.** Space filling models for asymmetrical azines **3–5**. The **a**-, **b**-, and **c**-structures are shown from left to right.



**FIGURE 3.** Ball-and-stick models are shown for asymmetrical azines **1a–5a** in a perspective that best illustrates that the N—N conformation and the phenyl twists act in concert to produce the largest possible twist between the planes of the benzene.

**TABLE II.**  
Energies and Dipole Moments of Asymmetrical 4'-Halogeno-4-methoxyacetophenone Azines as a Function of C=N—N=C Dihedral Angle.

MeO		$\angle\text{CNNC}(\tau)$	Sym.	$E_{\text{tot}}$	$E_{\text{rel}}$	VZPE	NIMAG	$\mu_{\text{calc.}}$
F	<b>1a</b>	165.0	C <sub>1</sub>	-936.809247				2.73
	<b>1b</b>	180	C <sub>1</sub>	-936.809084	0.10	206.06	0	2.80
	<b>1c</b>	180	C <sub>s</sub>	-936.808964	0.18	206.10	2	2.81
Cl	<b>2a</b>	164.7	C <sub>1</sub>	-1296.857775		205.10	0	3.37
	<b>2b</b>	180	C <sub>1</sub>	-1296.857605	0.11	205.10	0	3.44
	<b>2c</b>	180	C <sub>s</sub>	-1296.857462	0.20	205.14	2	3.46
Br	<b>3a</b>	164.7	C <sub>1</sub>	-3407.192021		204.74	0	3.52
	<b>3b</b>	180	C <sub>1</sub>	-3407.191851	0.11	204.75	0	3.59
	<b>3c</b>	180	C <sub>s</sub>	-3407.191705	0.20	204.79	2	3.61
	<b>3d</b>	137.5	C <sub>1</sub>	-3407.151140	25.65			2.80
	<b>3d'</b>	136.1	C <sub>1</sub>	-3407.168101	15.01			3.05
CN	<b>4a</b>	164.4	C <sub>1</sub>	-929.693092		210.67	0	6.56
	<b>4b</b>	180	C <sub>1</sub>	-929.692916	0.11			6.62
	<b>4c</b>	180	C <sub>s</sub>	-929.692719	0.23			6.66
	<b>4d</b>	117.9	C <sub>1</sub>	-929.679215	8.71			7.20
NO <sub>2</sub>	<b>5a</b>	164.4	C <sub>1</sub>	-1041.429459		213.81	0	7.01
	<b>5b</b>	180.0	C <sub>1</sub>	-1041.429288	0.11			7.07
	<b>5c</b>	180.0	C <sub>s</sub>	-1041.429067	0.25	213.88	2	7.13
	<b>5d</b>	134.0	C <sub>1</sub>	-1041.411750	11.11			

<sup>a</sup> Total energies in atomic units. Relative energies and VZPE in kilocalories per mole. Dipole moments in Debye.

CN, and NO<sub>2</sub> groups, respectively, are shown in Table I. Considering the standard deviations, one must conclude that no structural effects of azine asymmetry are manifested either in the methoxy-substituted or in the other fragments. Analysis of

the parameters describing the azine fragments leads to the same conclusion: The structural parameters of 2–5 do not show any significant manifestation of special electronic interactions over the N-perturbed extended  $\pi$ -system to be associated

**TABLE III.**  
Selected Structural Parameters of 4'-Halogen- or Nitro-substituted 4-Methoxyacetophenone Azine.

	$\tau$	$\phi_A$	$\phi_B$	$\theta_A$	$\theta_B$	C=N <sub>A</sub>	C=N <sub>B</sub>	N—N	C—C <sub>A</sub>	C—C <sub>B</sub>	C—O	C—X
<b>1a</b>	165.0	15.6	16.9	2.7	2.5	1.267	1.265	1.377	1.491	1.494	1.346	1.329
<b>1b</b>	180.0	13.3	15.2	0.3	0.3	1.267	1.266	1.377	1.491	1.494	1.345	1.329
<b>1c</b>	180.0	0.0	0.0	0.0	0.0	1.268	1.266	1.376	1.492	1.495	1.345	1.329
<b>2a</b>	164.7	15.5	18.0	2.7	2.4	1.267	1.265	1.377	1.490	1.495	1.345	1.743
<b>2b</b>	180.0	13.2	16.8	0.3	0.3	1.268	1.265	1.377	1.490	1.495	1.345	1.743
<b>2c</b>	180.0	0.0	0.0	0.0	0.0	1.268	1.265	1.376	1.491	1.496	1.345	1.743
<b>3a</b>	164.7	15.4	18.3	2.7	2.3	1.267	1.264	1.376	1.490	1.495	1.345	1.900
<b>3b</b>	180.0	12.9	17.0	0.3	0.3	1.268	1.265	1.377	1.490	1.495	1.345	1.900
<b>3c</b>	180.0	0.0	0.0	0.0	0.0	1.268	1.265	1.376	1.491	1.497	1.345	1.900
<b>4a</b>	164.4	15.2	19.9	2.8	2.2	1.268	1.264	1.376	1.489	1.496	1.344	1.445
<b>4b</b>	180.0	12.5	19.4	0.2	0.2	1.269	1.264	1.376	1.490	1.496	1.344	1.444
<b>4c</b>	180.0	0.0	0.0	0.0	0.0	1.269	1.265	1.375	1.490	1.498	1.344	1.444
<b>5a</b>	164.4	15.0	20.6	-2.8	-2.0	1.268	1.264	1.375	1.489	1.496	1.344	1.457
<b>5b</b>	180.0	12.0	20.3	0.0	0.0	1.269	1.264	1.376	1.489	1.496	1.344	1.457
<b>5c</b>	180.0	0.0	0.0	0.0	0.0	1.269	1.264	1.375	1.490	1.500	1.344	1.457

<sup>a</sup> Bond lengths in angstroms and bond angles in degrees.

with asymmetrization. Even with the existence of this best possible reference data set, the unambiguous identification of intrinsic features remains complicated by packing effects. Our discussion of the polymorphs of the *para*-methylacetophenone azine<sup>19</sup> points out that anisotropic environmental effects might result in distortions that are larger than the structural manifestations of the intramolecular electronic effects.

### CONFORMATIONAL PROPERTIES OF ISOLATED ASYMMETRICAL ACETOPHENONE AZINES

For each of the asymmetrical azines 1–5, we optimized the structure completely (**a**-structure) and with the constraints of  $\tau = 180^\circ$  (but the phenyl groups are still allowed to be out of plane, **b**-structure) and of  $C_s$ -symmetry (**c**-structure). Molecular models depicted in Figure 2 for some of the molecules and ball-and-stick models of **1a–5a** are depicted in Figure 3 in a “near Newman projection” down the N—N bond. For **3–5**, we also computed the energy based on the structures determined by the x-ray analysis and these data are included in Table II as the entries for the **d**-structures. The entries **3d** and **3d'** refer to the crystallographically independent molecules in crystals of **3**. None of the azines 1–5 is planar and the *trans-gauche* **a**-structures are the most stable structures in all cases. Yet, the constraints imposed on the **b**- and **c**-structures have hardly any significant consequences on energies ( $< 0.3$  kcal/mol). In light of the shallow nature of the potential energy surface

with regard to twists about the N—N and Ph—C bonds, it is not surprising, therefore, to find large differences between the N—N conformations of isolated azines and their crystal structure geometries.

Selected structural parameters are summarized in Table III and the dihedral angles  $\phi$  and  $\theta$  are defined as shown in the structural drawing given in the introduction. Note, in particular, and Figure 3 brings this feature very well to the fore, that the directions of the phenyl rotations are such that they result, in concert with the N—N *gauche* conformations, in the largest possible angle between the planes of the two benzene rings in each molecule. Because the N—N and the two C—C<sub>ipso</sub> bonds are nearly colinear, the angle  $\omega$  between the benzene planes is well approximated by the sum of  $(180 - \tau)$  and the  $\phi_i$  angles. In this way, we compute  $\omega$  angles of  $47$ – $52^\circ$  for **1a–5a** and these angles become even higher in the solids. It is this feature that makes azines so particularly valuable in crystal engineering as this facile twisting of the two benzene rings within each azine can be recognized as a prerequisite for the kinds of arene–arene T-contacts that bring about the intermolecular interactions in the crystals of **2** and **3**.

### ASYMMETRIZATION EFFECTS ON STRUCTURES OF ISOLATED ACETOPHENONE AZINES

In Table IV, we present a comparison of critical structural data of the asymmetric azines with reference to the symmetrical azines. The information

**TABLE IV.** Comparison of Theoretical Structural Parameters—Symmetrical versus Asymmetrical Acetophenone Azines.

	Asymmetrical, <sup>b</sup> MeO—X					Symmetrical, X—X					
	X = F	X = Cl	X = Br	X = CN	X = NO <sub>2</sub>	MeO	F	Cl	Br	CN	NO <sub>2</sub>
X—C	1.329	1.743	1.900	1.445	1.457		1.329	1.742	1.899	1.445	1.458
O—C	1.346	1.345	1.345	1.344	1.344	1.346					
N—N	1.377	1.377	1.376	1.376	1.375	1.377	1.377	1.376	1.376	1.376	1.375
N=C <sub>A</sub>	1.267	1.267	1.267	1.268	1.268	1.266					
N=C <sub>B</sub>	1.265	1.265	1.264	1.264	1.264		1.266	1.265	1.265	1.265	1.264
C <sub>ipso</sub> —C <sub>A</sub>	1.491	1.490	1.490	1.489	1.489	1.491					
C <sub>ipso</sub> —C <sub>B</sub>	1.494	1.495	1.495	1.496	1.496		1.493	1.494	1.494	1.496	1.496
$\tau$	165.0	164.7	164.7	164.4	164.4	165.9	164.2	163.1	162.9	161.4	–160.8
$\phi_A$	15.6	15.5	15.4	15.2	–15.0	15.6					
$\phi_B$	16.9	18.0	18.3	19.9	–20.6		17.1	18.3	18.5	20.6	21.6

<sup>a</sup> Optimized at RHF/6-31G\* and all electron double- $\zeta$  basis set for Br.

<sup>b</sup> A and B refer to the fragments with MeO and X, respectively.

provided in Table IV is similar to the information in Table I, but the data in Table IV are derived for the isolated molecules and these data reflect nothing but intrinsic effects. Clearly, if there existed any significance to the direct conjugative interactions between the donor and the acceptor—if there were significant contributions of the kind of resonance forms C—then such an interaction should manifest itself in X-dependent effects on the C=N and N—N bond lengths. Yet, the computed structures do not show such effects for the planar c-structures. As can be seen in Table III, the C=N and N—N distances differ hardly at all through the entire set of molecules. Even more compelling is the fact that these C=N and N—N distances do not vary with the dihedral angle  $\tau$ . Perhaps the best argument for the presence or absence of structural manifestation of conjugative interactions in the ground states is made by the comparison between the symmetrical and the asymmetrical azines. The data collected in Table IV allow for this consideration. In light of these data, a convincing case can be made that there is no significant structural difference whatsoever between the C=N and N—N bonds of the symmetrical and asymmetrical azines. All of the bond lengths X—C and MeO—C are affected by less than 0.001 Å as a result of asymmetrization.

#### NATURAL POPULATION ANALYSIS OF ASYMMETRIC ACETOPHENONE AZINES

Although the analyses make a clear and strong case for the absence of significant asymmetrization effects in the ground state structures of the azines, electronic effects associated with the asymmetrization might still occur. To explore this possibility, we determined the natural populations for the equilibrium structures and of the planar structures of 1–5, and the most pertinent results are shown in Table V. In Table V, the columns in sections A and B refer to the atoms in the methoxy- or X-substituted fragments, respectively. Irrespective of the conformation (a vs. c) and the nature of X, there are no changes in the population data of the methoxy-benzene system or the azine bridge. Figure 4 illustrates this important finding in a com-

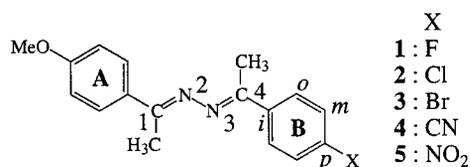


TABLE V.  
Natural Population Analyses of 4'-Halogeno-4-Methoxyacetophenone Azine.

	A							B										
	C1	N2	N3	C4	C <sub>i</sub>	C <sub>o</sub>	C <sub>m</sub>	C <sub>p</sub>	O	C <sub>i</sub>	C <sub>o</sub>	C <sub>m</sub>	C <sub>p</sub>	X				
1a	0.36	-0.38	-0.37	0.35	-0.15	-0.13	-0.17	-0.34	-0.29	0.40	-0.61	-0.13	-0.15	-0.18	-0.31	-0.32	0.50	-0.39
1c	0.37	-0.39	-0.37	0.35	-0.16	-0.13	-0.17	-0.34	-0.29	0.41	-0.61	-0.13	-0.15	-0.18	-0.31	-0.32	0.50	-0.39
2a	0.37	-0.39	-0.36	0.34	-0.16	-0.13	-0.17	-0.34	-0.29	0.40	-0.61	-0.10	-0.17	-0.19	-0.24	-0.24	-0.03	-0.02
2c	0.37	-0.39	-0.37	0.34	-0.16	-0.13	-0.17	-0.34	-0.29	0.41	-0.61	-0.10	-0.16	-0.19	-0.24	-0.24	-0.03	-0.02
3a	0.37	-0.39	-0.36	0.34	-0.16	-0.13	-0.17	-0.34	-0.29	0.40	-0.61	-0.10	-0.17	-0.20	-0.24	-0.24	-0.12	0.05
3c	0.37	-0.39	-0.36	0.34	-0.16	-0.13	-0.17	-0.34	-0.29	0.41	-0.61	-0.10	-0.17	-0.20	-0.24	-0.24	-0.11	0.05
4a	0.37	-0.39	-0.35	0.33	-0.16	-0.13	-0.17	-0.34	-0.29	0.41	-0.61	-0.06	-0.19	-0.22	-0.17	-0.17	-0.17	-0.05
4c	0.38	-0.39	-0.35	0.33	-0.16	-0.13	-0.17	-0.34	-0.29	0.41	-0.61	-0.06	-0.19	-0.22	-0.17	-0.17	-0.17	-0.05
5a	0.38	-0.39	-0.35	0.33	-0.16	-0.13	-0.17	-0.34	-0.29	0.41	-0.61	-0.04	-0.20	-0.23	-0.19	-0.18	0.03	-0.27
5c	0.38	-0.40	-0.35	0.33	-0.16	-0.13	-0.16	-0.34	-0.29	0.41	-0.61	-0.05	-0.19	-0.23	-0.19	-0.18	0.04	-0.27

No change, no matter what conformation and or nature of X  
 \_\_\_\_\_ Very Small Change

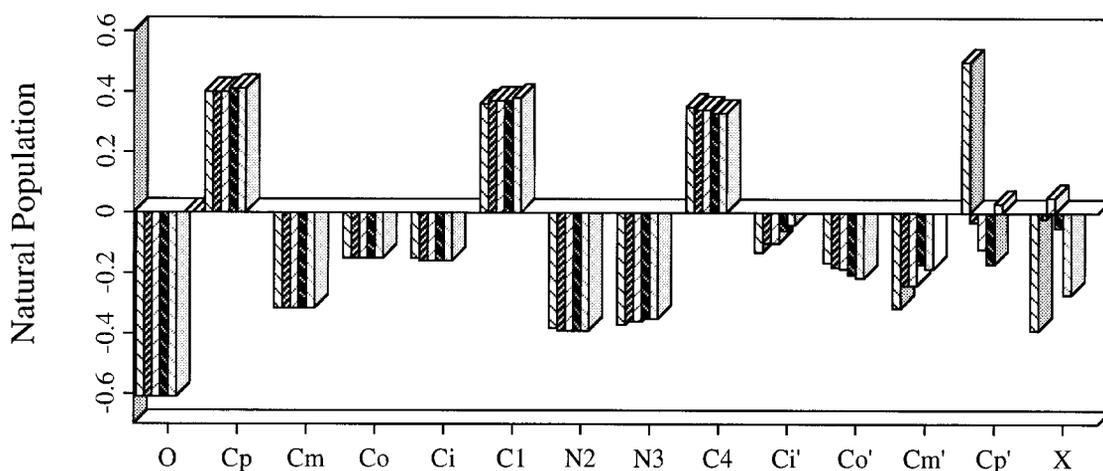
elling fashion for the **a**-structures. There are population changes in the **B** ring as the *X* group varies and these can be quite significant, but—and this is what matters in the present context—the electronic effects of the *X*-substituents are felt hardly at all beyond the C-atom that attaches the **B**-ring to the spacer.

### DIPOLE MOMENTS OF ASYMMETRIC ACETOPHENONE AZINES

The computed dipole moments of azines 1–5 are listed in the last column of Table II. The dipole moment of *para*-nitroaniline, PNA, is roughly 7 Debye and may serve as a reference. The substituents in PNA are comparable to the substituents in azine 5, but 5 has a dipole moment that is just about the same as that of PNA despite the much greater distance between the donor and the acceptor in 5. On the premise that the dipole moment represents an indicator of conjugative interaction and charge transfer between the donor and the acceptor in the ground state, one would have expected a much larger dipole moment for 5. Following this logic, one would then have to conclude that, indeed, the azine spacer acts as an efficient “conjugation stopper.” The azines realize comparatively small dipole moments and the polarity can be reduced even below 3 Debye via a suitable selection of the *X*-groups. The dipole moments of azines 2 and 3, the ones for which the near perfect dipole parallel alignment in the solid has been achieved, are about 3.5 Debye.

### Conclusion

It has been our objective to design asymmetric donor–acceptor-substituted  $\pi$ -conjugated systems with low dipole moments and structural components that favor parallel alignment of neighboring molecules. The design features not only should provide NLO properties but also should make it possible to obtain dipole parallel-aligned lattices of the pure molecular material. To realize low dipoles in the ground state, while still allowing large charge transfers along the molecular axes in the virtual excited states, we chose azine spacers between asymmetrically substituted benzenes. The azine functional group effectively provides two directly coupled and oppositely oriented acceptors and partitions the molecule into a short donor–acceptor system that is linked to a quadrupolar acceptor–acceptor system. The results presented for 1–5 show that we have accomplished our original goal of designing  $\pi$ -conjugated donor–acceptor materials with relatively small dipole moments and it seems that the notion of the “conjugation stopper” is useful. The conformational properties about the N–N and the Ph–C bonds, the comparative analysis between symmetrical and asymmetrical azines, and the population analysis all show no significant evidence for conjugation over the azine bridge. This finding parallels studies of donor–acceptor-substituted diphenylacetylenes.<sup>28</sup> This lack of conjugation and the nonplanarity of



**FIGURE 4.** Graphical illustration shows in a compelling fashion that the charge distribution in the MeO-substituted phenyl ring is essentially independent of the identity of the substituent attached to the other benzene ring. From left to right, the data refer to compounds 1a–5a.

the azines do not affect the hyperpolarizabilities. At the same time, in light of the above analysis, it is also becoming apparent that charge transfer between the donor and the acceptor contributes to the dipole moment much less than is generally assumed. We are now in the process of comparing the electronic structures of azines and butadienes to delineate the inductive and mesomeric contributions to the ground state dipole moments as the result of asymmetrization.

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