Conformational Studies of the *N*-(3-Halobenzylidene)-3-haloaniline System. Part 2.[†] Molecular Energetics

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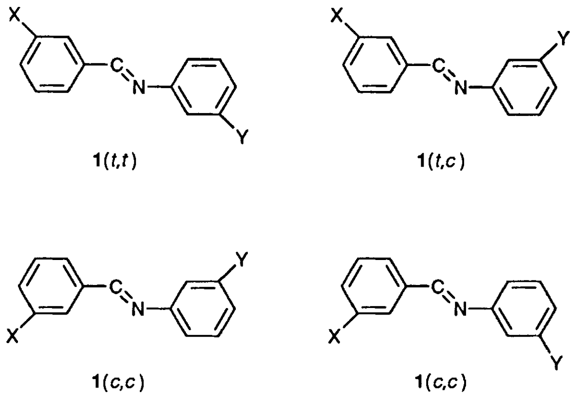
Molecular energetics of the *N*-(3-halobenzylidene)-3-haloanilines have been studied, using semiempirical molecular orbital calculations, and served as a basis for comparison the results from a gas-phase electron diffraction (GED) experiment. As the molecule contains a π-electronic system—a phenyl ring linked through a single bond to a double bond—which has proved problematic for semiempirical methods, a number of these have been tested: AM1, MINDO/3, PM3 and MNDO in addition to molecular mechanics [CAChe-MM2 and MM2(91)], and this study serves as a critical comparison and evaluation of these methods for treating such a classic molecular electronic linkage. The computational methods that were found to be suitable for the *N*-benzylideneaniline molecule were AM1 and MM2(91). For two of the title derivatives there is a significant difference between the conformation found in the crystal structure and that determined by GED in concert with the calculations based on the AM1 method.

> '... To summarize, it must be emphasized once again that the crystalline field does not change the bond lengths and valence angles of organic molecules. The major effect of the crystalline field on the shape of the molecule consists in provoking such rotations about single bonds as are most favourable for packing. However, these rotations can take place only if the optimum conformation of the molecule is unstrained.'

Kitaigorodskii[1] used the term 'crystalline field' to describe the effect of packing of molecules in the solid state on their molecular conformation. This term is more commonly referred to now as 'crystal forces' ('intermolecular interactions', 'intermolecular forces' and 'packing forces' are also commonly used terms). The influence of crystal forces on molecular conformation has been increasingly investigated in the last three decades, by computational and experimental methods.[2]

Kitaigorodskii[1] suggested four approaches to investigate the relationship between crystal forces and molecular conformation: (1) comparison of the structures of gaseous and crystalline molecules; (2) comparison of the geometries of crystallographically independent molecules in the same crystal; (3) analysis of the structure of a molecule whose symmetry in a crystal is lower than that of the free molecule; (4) comparison of molecules in different polymorphic modifications. In this paper we have chosen the first approach, that of comparing the solid state conformation with both the computed free molecule conformation and the gas phase conformation, as obtained by gas phase electron diffraction (GED).

In the first paper in this series[3] we presented the crystal structures of four derivatives of *N*-(3-halobenzylidene)-3-haloanilines **1** (**a**, X = Br, Y = Cl; **b**, X = Y = Br; **c**, X = Cl, Y = Br; **d**, X = Y = Cl), in which four extreme situations for the two halogen substituents may be defined in Fig. 1. The observed crystal conformations of these four derivatives are *c,c* for compounds **1b–d** and *t,t* for compound **1a**. The difference in conformation between the first three derivatives on the one hand and the fourth on the other hand might be attributed to crystal forces.



1(*t,t*) **1**(*t,c*) **1**(*c,c*) **1**(*c,c*)

Fig. 1

Prior to investigating this question, however, it is necessary to determine if there is any energetic preference in the free molecule as a function of the substituents, which could result in the observed difference between the solid state molecular conformation of **1a** and the other three.

The investigation of a preferred conformation requires a mapping of the multidimensional conformational energy surface. In **1** the problem is considerably reduced since there are essentially only two conformational parameters, the two exocyclic torsion angles.

The parent molecule, *N*-benzylideneaniline (**2**), was and still is a target molecule for conformational studies.[4] This molecule consists of three π-systems linked by single bonds. Interest in the molecule was aroused mainly due to the different electronic spectrum of **2** compared to its two isoelectronic analogues (*E*)-azobenzene and (*E*)-stilbene **3** and **4**. The latter were found to be planar in the solid state[5] and in solution,[6] while **2** is generally not planar in those phases.[7] It is noteworthy that all three have been shown to have a non-planar conformation in the gas-phase, although the extent of rotation about the C–N single bond in **2** is larger (55°)[8] than the estimated rotations of the phenyl groups in **3** and **4** (up to 30°).[9]

N-Benzylideneaniline (**2**) and its derivatives have been the

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[†] Part 1. Ref. 3.

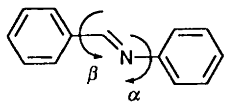
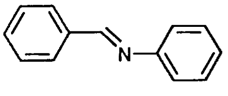


Fig. 2 *N*-Benzylideneaniline: definition of the two exocyclic torsion angles



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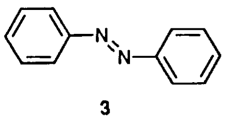

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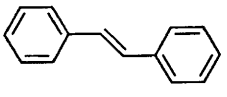

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Table 1 Experimental data for gas electron diffraction of structures of **1a** and **b**

	1a	**1b**
Voltage/KV	40	40
Wavelength/Å	0.060474	0.060278
No. of plates (50 cm)	3	7
No. of plates (19 cm)	5	7
Nozzle temperature/°C	172	180

Table 2 Experimental and calculated values of torsion angles (°) for *N*-benzylideneaniline

Experiment or computation technique	β	α
X-Ray diffraction[a]	−10.3	55.2
Gas electron diffraction[b]	0(15)	52(5)
NDDO[c]	0	60
CNDO/S[d]	0	30–35
PCILO[e]	0	36
π-electron + n.b.	0	37
Interaction[f]		
STO-4G[g]	0	45
CNDO/2[h]	30	90
AM1[i]	3.7	−30.6
MM2-CAChe[i]	0	0
MM2(91)[i,j]	0	0
MM2(91)[i,k]	1.5	40.4
PM3[i]	0	0
MINDO/3[i]	90	90
MNDO[i]	90	90

[a] See ref. 7*a*. [b] See ref. 8. [c] See ref. 28. [d] See ref. 29. [e] See ref. 30. [f] See ref. 31. [g] See ref. 4*d*. [h] See ref. 13. [i] Present work. [j] Calculated as a non-conjugated system. [k] Calculated as a conjugated system.

subject of a number of investigations in the past few years, including studies employing IR[10] and a variety of NMR studies,[11] X-ray crystallography[12] and molecular orbital calculations.[13]

Although molecular mechanics and molecular orbital methods have matured considerably over the past two decades, there still remain a number of classic problem situations which are not treated by all these methods either uniformly or correctly. One of those situations involves two or more π systems linked by a single bond, which have been notoriously challenging, for instance for some semi-empirical molecular orbital methods.[14]

In this study **2** served as the touchstone for two different computational methods for investigating the molecular energetics with particular emphasis on the two linked π-systems noted above: molecular mechanics (MM2), and semi-empirical quantum mechanical molecular orbitals (AM1, PM3, MNDO, MINDO/3). *Ab initio* calculations were not tested due to the large number of electrons of the Br and Cl substituents on **1**.

Experimental

Methods of Computation.—AM1[15] semi-empirical calculations were carried out using the AMPAC package.[16] PM3,[17] MINDO/3[18] and MNDO[19] methods were applied using CAChe MOPAC[20] with CAChe interface on a Macintosh platform. Two versions of MM2[21] were used, the CAChe MM2 and MM2(91)[22]—Molecular mechanics for MacMimic for Macintosh II.

Gas Electron Diffraction.—The electron diffraction photographs were recorded on the EG-100A apparatus of the Budapest Group.[23] A stainless steel nozzle system was used somewhat modified from previous design.[24] The experimental conditions are summarized in Table 1.

A least-squares refinement of the geometrical and vibrational parameters was based on the molecular intensities.[25] The atomic inelastic and elastic scattering factors and phase shifts were taken from ref. 26. An estimated force field was used to calculate mean amplitudes of vibrations, some of which then were refined while others were fixed to values of the initial estimates. Some of the starting values of the geometrical parameters were taken from the electron diffraction study of *N*-benzylideneaniline (**2**) itself.[8]

Results and Discussion

Molecular Orbital Calculations.—*Molecular conformation of the* N-*benzylideneaniline molecule by comparison methods.* The two exocyclic torsion angles α and β are defined in Fig. 2; some previously reported experimental and calculated values for them are summarized in Table 2. There is a wide variation in the results obtained, with quite a few methods yielding limiting values of either 0° or 90° for one or both of the conformational angles.

The experimental molecular conformation obtained from both gas phase electron diffraction[8] and X-ray diffraction[7] consists of a planar region that contains the benzylidene ring and the C=N double bond ($\beta \approx$ 0–10°) while the aniline ring is twisted relative to the double bond ($\alpha \approx 50°$).

CAChe-MM2 calculations failed to produce the non-planar conformation of the unsubstituted *N*-benzylideneaniline, and the conformation obtained from the minimization was planar ($\alpha \approx \beta \approx 0°$). On the other hand MM2(91) produced a molecular conformation that is very close to the gas phase conformation ($\alpha \approx 40°$, $\beta \approx 0°$). This resultant difference due to changing of the force field was found also in calculations using CAChe-MM2 on anilides.[27] In that case the CAChe-MM2 produced incorrect minimal conformation, as here. In the PM3 calculations, it is clear that the π-electron energy is weighted more than the non-bonded interactions, which results in a predicted planar conformation of the molecule. Actually the potential energy for the *N*-benzylideneaniline is rather flat ($\approx$ 0.5 kcal mol^{-1} difference between maximum and minimum points), and consists of two local minima in addition to that at $\alpha \approx 0°$, in the range of $\alpha \approx$ 40–60° and $\alpha \approx$ 130–140°.

On the other hand MNDO and MINDO/3 calculations overestimate the delocalization of the nitrogen lone-pair electrons into the aniline ring, to give a value of $\alpha \approx 90°$. Both also break the conjugation between the benzylidene part and the double

Table 3 Molecular conformation and energy of the molecule **1d** using AM1

	Min1	Min2	Min3	Min4
E/kcal mol^{-1}	60.01	60.11	60.18	60.33
α (°)	34.5	34.8	147.8	147.6
β (°)	-174.0	5.7	174.3	-3.0
Conf.	*t,c*	*c,c*	*t,t*	*c,t*

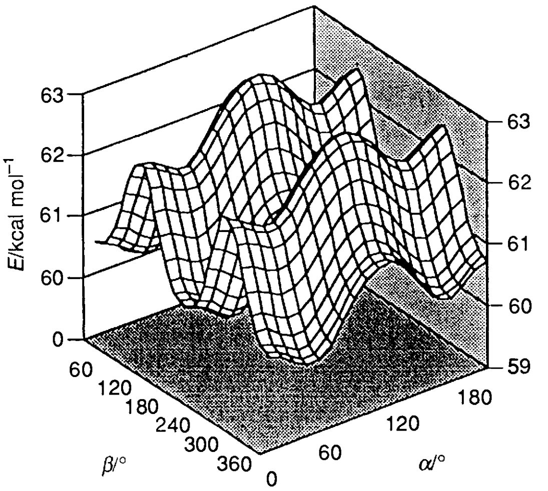

Fig. 3 Three dimensional graph of the potential energy surface of **1d** obtained from AM1 calculations

bond, resulting in a β value of 90°. These two methods thus fail completely to predict the conformation of **2**. A recent calculation[13] performed using the CNDO/2 method surprisingly gives a conformation of $\alpha = 90°$ and $\beta = 30°$ as the lowest minimum energy conformation.

The *ab initio* calculation with an STO-4G basis set[4d] gives a α value of 45°, and a β value of 0°, a conformation that matches that found experimentally.

The semi-empirical molecular orbitals methods that yield conformation for **2** approximating the experimental and *ab initio* ones, are NDDO,[28] CNDO/S,[29] PCILO,[30] a model combining π-electron energy and non-bonded interactions,[31] and AM1, with α ranging from 30° to 60° and $\beta \approx 0°$. The AM1 method was chosen for application to the derivatives of **1** studied here.

Calculation of the potential energy surface. The conformational behaviour of the *N*-(3-halobenzylidene)-3-haloaniline was investigated by computing the potential energy surface as a function of α and β using the AM1 method. The conformational space was sampled by varying α and β in steps of 10°, for $0° < \alpha < 180°$, $0° < \beta < 360°$. At each point a full geometry optimization was carried out.

For **1d** four local minima were obtained and are given in Table 3. The lowest of these is 60.01 kcal mol^{-1} corresponding to $\alpha = 34.5°$, $\beta = 174.0°$. The maximum of the energy potential surface is in the range of $\alpha = 90$–$100°$ and $\beta = 90°$, with the respective energy of 62.98 kcal mol^{-1}, which is about 3 kcal mol^{-1} higher than the energy of the lowest minimum in the energy surface. In this conformation the π-electron conjugation is broken because both rings are perpendicular to the double bond. Consistent with the results obtained on other benzylideneanilines, the energy of the planar conformation (60.49 kcal mol^{-1}) is 0.5 kcal mol^{-1} higher than the lowest minimum of the energy surface.

The three dimensional graph of the potential energy surface is shown in Fig. 3. Two cross-sections were taken from the graph at $\beta = 0°$, and at $\alpha = 0°$ [Figs. 4(*a*) and (*b*)] to emphasize the different energetic behaviour of the two paths. There is a strong preference for the benzylidene ring to be planar, so that a perturbation of β from 0° results in an increase in energy, and while changing α from 0° to higher values leads to a decrease in energy. The energetic behaviour of α is consistent with the model of steric interference between the *ortho* hydrogen of the anilinic part and the hydrogen of the bridge.[4d]

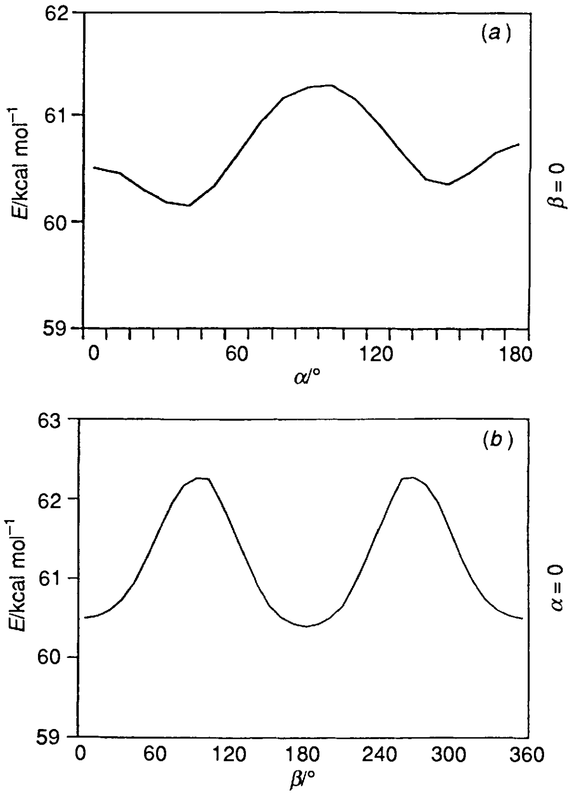

Fig. 4 (*a*) Cross-section of Fig. 3 at $\beta = 0°$; (*b*) cross-section of Fig. 3 at $\alpha = 0°$

Energy calculations of the four minima for the remaining derivatives. After finding the local minima in **1d**, we carried out a computation of the three remaining molecules **1a–c**. The starting geometries for the geometry optimization for each molecular conformation, *e.g. t,c*, *c,c*, *c,t* and *t,t*, were those obtained from the calculation of the potential energy surface of **1d**. The results are shown in Table 4. It can be seen that there is a consistency among the four compounds studied in the order of the molecular conformations in spite of the fact that the energy differences between them are very small. The *t,c* conformation has the lowest energy for all the derivatives, while the *c,t* conformation has the highest one. The energies corresponding to the observed molecular conformations *c,c* and *t,t* have median values.

It should be noted at this point that it has already been shown that AM1 under-estimates both the rotational barriers of conjugated systems, and the energy differences between conformers. However, at the same time it predicts well the conformational preference, and the rotational barrier can be scaled up to correlate with *ab initio* or experimental values.[14a,d,e] These characteristics of the AM1 method are confirmed here, and based on this clarification, we can assume that there *is* an energetic preference in the ordering of the four possible conformations, and that *t,c* is indeed the preferred conformation in the gas phase.

From the relative magnitudes of the minima and the consistency among the four compounds it is clear that there is no molecular energetic preference. Thus, the difference in the observed solid state molecular conformation of **1a**, *t,t*, from that found for the other three compounds *c,c*, must be based essentially on crystal forces.

Table 4 Molecular energetics of **1a–c** (energy in kcal mol^{-1}) using AM1

	1a				**1b**				**1c**			
	E	α (°)	β (°)	Conf.	*E*	α (°)	β (°)	Conf.	*E*	α (°)	β (°)	Conf.
Min1	71.91	34.8	−173.0	*c,t*	83.88	34.8	−172.4	*t,c*	71.97	34.8	−173.6	*t,c*
Min2	72.08	34.2	6.0	*c,c*	84.03	34.4	1.5	*c,c*	72.07	34.5	6.3	*c,c*
Min3	72.08	147.8	174.9	*t,t*	84.07	148.3	174.9	*t,t*	72.16	148.2	174.9	*t,t*
Min4	72.28	148.3	−6.9	*c,t*	84.26	147.6	−9.2	*c,t*	72.31	148.3	−7.1	*c,t*

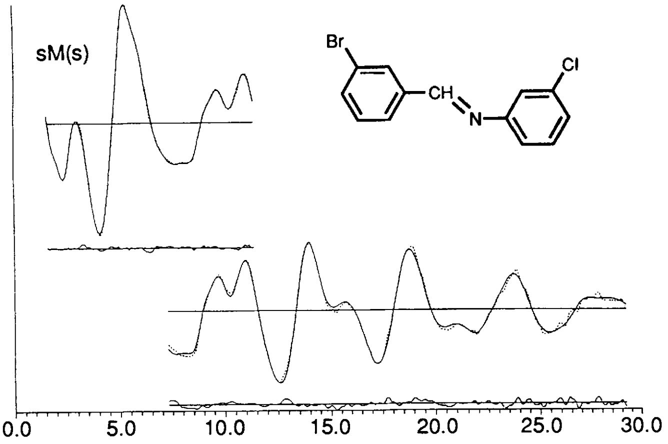

Fig. 5 Experimental and calculated molecular intensities (top) and the difference curve (bottom) for **1a**

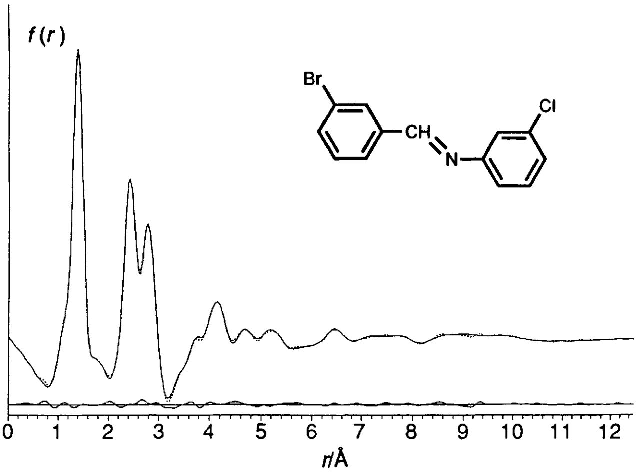

Fig. 7 Experimental and calculated radial distributions (top) and the difference curve (bottom) for **1a**

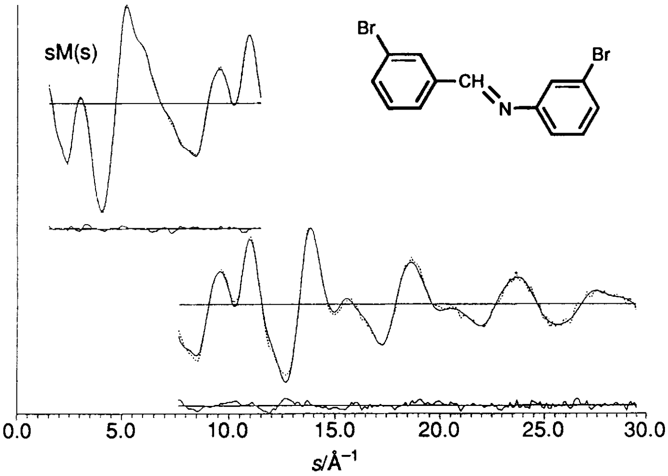

Fig. 6 Experimental and calculated molecular intensities (top) and the difference curve (bottom) for **1b**

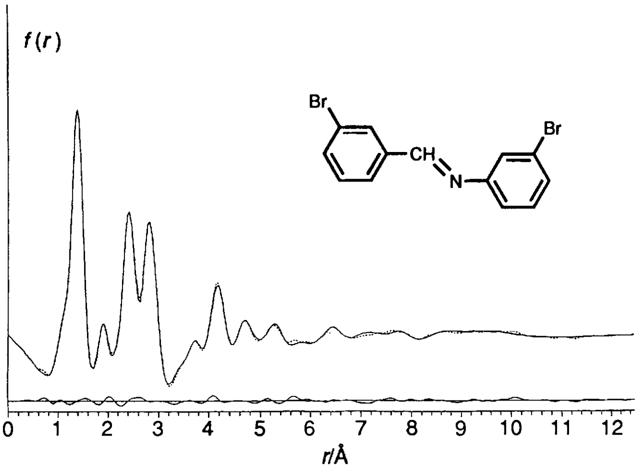

Fig. 8 Experimental and calculated radial distributions (top) and the difference curve (bottom) for **1b**

Estimation of the energy difference between the two molecular conformations found in the disordered structures. Three of the four derivatives exhibit disorder in the solid state.[3] The molecular orbital calculations allow us to estimate the energy difference between two molecular conformations obtained from the model of disorder.

The model of the disorder in **1c** and **d** which is described in more detail in the previous paper[3] adds a degree of complexity to this discussion. Usually the disorder in substituted aromatic compounds is a crystallographic one, meaning that it results from the location of the molecule on a special position of the space group which results in higher apparent molecular symmetry than can be attributed to the molecule. However in the cases under consideration, the molecules are located in general crystallographic position, *e.g.* there is no constraining symmetry relationship between the two parts of the molecule. The electron density maps of the disordered structures **1d** and **c**[3] result from the combination of two molecular conformations. It was therefore necessary to estimate the energy difference between the two conformations in order to examine the model of disorder.[3]

In structure **1d** all the atomic parameters were refined including the hydrogen atom on the bridge. On the other hand in structure **1c** two molecular conformations were indicated by the electron density map, were weighted 67% and 33%, the hydrogen on the bridge of the lower occupancy factor was not refined. Since the calculation for estimation of the energy difference between the two conformations requires full geometry data, the AM1 calculations were carried out only on structure **1d**.

The starting geometry of each molecular conformation was taken from the crystal structure. Only the two phenyl rings with the halogen substituents were fully optimized while the bridge parameters, including bond lengths, bond angles and torsion

Table 5 Geometry parameters for **1a** and **b**; bond lengths (Å), bond angles and torsion angles (°), with their standard deviations from least squares refinement[a]

Parameter	**1a**	**1b**
C–H (mean)	1.095(4)	1.095(7)
C=N	1.281(7)	1.27(1)
C–C (ring, mean)	1.369(1)	1.369(1)
C–N	1.43(1)	1.43(2)
C–C	1.48(2)	1.47(3)
C–Cl	1.727(4)	—
C–Br	1.892(3)	1.890(2)
C–C–C=	121(1)	120(2)
C–C=N	120(2)	120(2)
C=N–C	114(1)	114(1)
N–C–C	120(1)	120(2)
C–C(=)–H	118(1)	118(1)
τ (C$_{ring}$–C)[b]	−157(5)	−157(8)
τ (N–C$_{ring}$)[c]	55(3)	52(7)

[a] The bridge atoms C^5–C^7=N^1–C^8 were assumed to be planar (for other assumptions, see text). Both $\tau = 0°$ correspond to a planar *c,c* conformation. [b] Noted earlier as β. [c] Noted earlier as α.

Table 6 Torsion angles (°) and *R*-factors from least-squares refinement of the four models

Model	τ (C$_{ring}$–C)	τ (N–C$_{ring}$)	R_{50}	R_{19}	R_{tot}
1a					
t,t	−165(4)	−122(2)	0.0457	0.0831	0.0649
c,c	15(5)	−43(3)	0.0459	0.0835	0.0652
t,c	−157(5)	55(3)	0.0283	0.0833	0.0592
c,t	−8(6)	−126(2)	0.0343	0.0826	0.0605
1b					
t,t	−174(6)	−124(3)	0.0661	0.139	0.105
c,c	20(6)	44(5)	0.0528	0.141	0.102
t,c	−157(5)	52(3)	0.0383	0.136	0.0951
c,t	−16(8)	−127(4)	0.0491	0.136	0.0977

angles, were fixed with the values obtained from the crystal structure.

The resultant energy difference between the two molecular conformations is about 1 kcal mol^{-1}, a value that is in the order of magnitude expected when disorder is present,[32] and of the energy difference between polymorphs,[33] and also with the difference in energy obtained from an *ab initio* calculation[4d] on **2** employing a STO-4G basis set.

Gas Electron Diffraction.—From the results presented in Tables 3 and 4, we have concluded that the order of molecular energetics is identical for the four derivatives, **1a–d**, and that on the basis of these calculations, the gas phase molecular conformation in all four is predicted to be *t,c*. We have carried out GED experiments on two derivatives, **1a** and **b**, which are the 'representatives' of the two different solid state observed conformations *t,t* and *c,c* respectively.

The experimental and calculated molecular intensities and the radial distributions are shown in Figs. 5–8. The bond lengths, bond angles and torsion angles resulting from the structure refinement are collected in Table 5. Not all the parameters listed could be refined simultaneously, some of them were refined one at a time, keeping the remainder constant. The standard deviations listed in Table 5 were obtained in a refinement involving all variables simultaneously with nearly zero shift. Table 6 lists the torsional angles and *R*-factors obtained for four models. It is clearly seen that the marked differences that are found in the R_{50} refer to the small-angle scattering and this is where the contribution of the longest internuclear distances that characterize the conformation occur. The choice of the *t,c* model as the conformer best approximating the experimental data is made primarily on the basis of the long camera range data. It is comforting that even the next best *c,t* model displays 17% (for the **1a**) and 22% (for the **1b**) worse agreement with the experimental data according to the R_{50}-factors than the *t,c* model. It is also seen that the **1b** data are generally of lesser quality than the **1a** data, as a result of the stronger atomic scattering of the two bromines in **1b**.

Molecular Orbital Calculation vs. *Gas Electron Diffraction*.—The GED determination of the molecular structure indicates that the preferred free molecule conformation is *t,c* for both **1a** and **b**, in concert with the AM1 calculations.

Due to the small energy differences between conformers a more precise model for refinement of the GED data would involve taking into account a weighted average of at least the four extreme conformers. Such a model, however, would involve the ratio of variables to observable which would be statistically unacceptable. The main structural parameters, however, are probably slightly sensitive to the conformational choice of model used in the refinement, especially in view of the rather large experimental uncertainties. As an alternative, we must refer to the results given in Table 6. The α and β values for the various models in **1a** and **b** are ranged between 43° to 58° and 6° to 23°, respectively (by looking at the absolute values of the angles). The AM1 results summarized in Tables 2 and 3 give $\alpha \simeq 35°$ and $\beta \simeq 3$–$10°$.

Although GED and AM1 yield different torsional angles, each technique gives the same two torsional angles for the two compounds. GED results show greater angles of torsion which may (or may not) be a consequence of averaging over intramolecular motion. The principal aim of this investigation was not to find the absolute values of α and β, but to obtain the gas phase conformation in terms of the relative positions of the halogen substituents, *e.g.* either *t,c* then *t,t*, *c,t* or *c,c*, for the four compounds, and to be able to examine various semi-empirical methods for reliability in predicting conformations about a single bond linking a double bond and a substituted phenyl group. For this purpose this study showed that the AM1 method appears to be the most suitable for calculating conformational preferences of conjugated systems of this type. The differences of the conformation noted in the crystal structures of **1a–d** are supposed to be due to intermolecular interactions, the study of which will be reported in a subsequent publication.

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