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Electronic Structure of 4,5-Bis(dimethylamino)fluorene. PE Spectroscopic Investigations

Rolf Gleiter,*† Wolfgang Schäfer,† Heinz A. Staab,*‡ and Thomas Saupe‡

Institut für Organische Chemie der Universität Heidelberg and Abteilung Organische Chemie, Max Planck Institut für medizinische Forschung, D-6900 Heidelberg, West Germany

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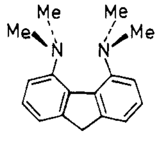
The He(I) photoelectron spectrum of 4,5-bis(dimethylamino)fluorene (1) has been recorded and compared with those of 4-(dimethylamino)- and 4-aminofluorene, 3 and 4, respectively. The assignment of the PE spectra is based on ZDO calculations and on the correlation of the bands. It is shown that the split between the two lone pairs of the dimethylamino groups in 1 amounts to 2.2 eV. MINDO/3 calculations on 1, 3, and 4 reproduce the PE results of 3 and 4 reasonably well but fail to reproduce the split of the lone pairs in 1.

Recently the synthesis of a new proton sponge, 4,5-bis(dimethylamino)fluorene (1) has been reported.[1] Model considerations based on planar molecules suggested that the distance between the two N centers (231 pm) should be closer than that in 1,8-bis(dimethylamino)naphthalene (2)[2] (245 pm). With these considerations in line are basicity measurements which reveal a pK_a value of about 13.5 for 1 and X-ray investigations on the perchlorate of 1 which demonstrate an actual N–N distance of 262.6 (2) pm.[1]

To contribute to the question of the electronic structure of 1 we have investigated the HE(I) photoelectron (PE) spectra of 1, 4-(dimethylamino)fluorene (3), and 4-aminofluorene (4).



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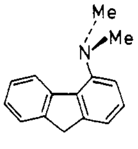

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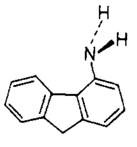

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In Figure 1 we show the PE spectra of 1, 3, and 4. The PE spectrum of 1 shows four peaks below 10 eV (bands 1–6). The first and fourth peaks are assigned to two transitions each since the area below the envelopes is about twice the area of band 3 or 4. In case of 3 and 4 we observe five bands clearly separated from the strongly overlapping bands below 10 or 10.5 eV, respectively. The measured ionization energies are collected in Table I.

Assignment of the PE Spectra

To assign the PE spectra we assume that the measured ionization energies, $I_{v,j}$, of the first bands can be set equal to the negative values of the orbital energies, $-\epsilon_j$. This approximation[3] assumes that the orbital wave functions which describe the ground state of a molecule are also valid to describe its ionic states. Numerous investigations on large organic systems have shown that this assumption holds quite well.

To assign the first few bands in the spectra we proceed in two ways, either by deriving the orbital energies via a ZDO model using basis orbital energies and resonance integrals from similar investigations or by using current semiempirical methods to calculate the orbital energies.

a. **ZDO Model.** Model considerations show that for steric reasons the dimethylamino groups in 1 are twisted considerably (>60°) out of the molecular plane. Therefore the overlap of the two nitrogen lone pairs at the dimethylamino groups with the π-system of the fluorene fragment can be neglected, which, in turn, allows us to treat both fragments separately.

Table I. Ionization Energies (eV) of 1, 3, and 4

compd	band	$I_{v,j}$	assignment
1 (C_{2v})	1	7.1	b_1 (n_-)
	2	7.3	a_2 (π)
	3	8.10	a_2 (π)
	4	8.89	b_2 (π)
	5	9.35	a_1 (n_+)
	6	9.5	b_2 (π)
3	1	7.5	π
	2	8.11	π
	3	8.70	"n"
	4	9.2	π
	5	9.70	π
4	1	7.6	π
	2	8.2	π
	3	8.85	π
	4	9.67	π
	5	10.4	π

We start our interpretation with the PE spectrum of fluorene (5),[4] which shows four bands below 10 eV. All four bands are assigned to ionization processes out of π-orbitals which belong to the irreducible representations A_2 and B_2. For our argumentation we will use the wave function of biphenyl calculated according to the HMO model.[5] The effect of the CH_2 group (inductive and hyperconjugative) is taken care of if we adopt the ionization energies of fluorene[4] as basis orbital energies. The HMO wave functions as well as the orbital energies used are shown in Figure 2. The effect of the strongly twisted dimethylamino groups in 1 we treat as an inductive perturbation. The correction terms, $\delta\epsilon_j$, of the orbital energies ϵ_j are derived according to (1).[6] In this equation c_{js} represents the AO coefficients at position 4 and 5, while c_{jt} represents the coefficients at the positions 3, 6, 11, and 12 of 5. For the parameters $\delta\alpha$ and m we adopt the values used by Maier[6] in his investigations of the PE spectrum of 2, i.e., $\delta\alpha = 1.9$ eV and $m = {}^1/_3$.

$$\delta\epsilon_j = \sum_s c_{js}^2\delta\alpha + \sum_t c_{jt}^2 m\delta\alpha \qquad (1)$$

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† Universität Heidelberg.

‡ Max Planck Institut.

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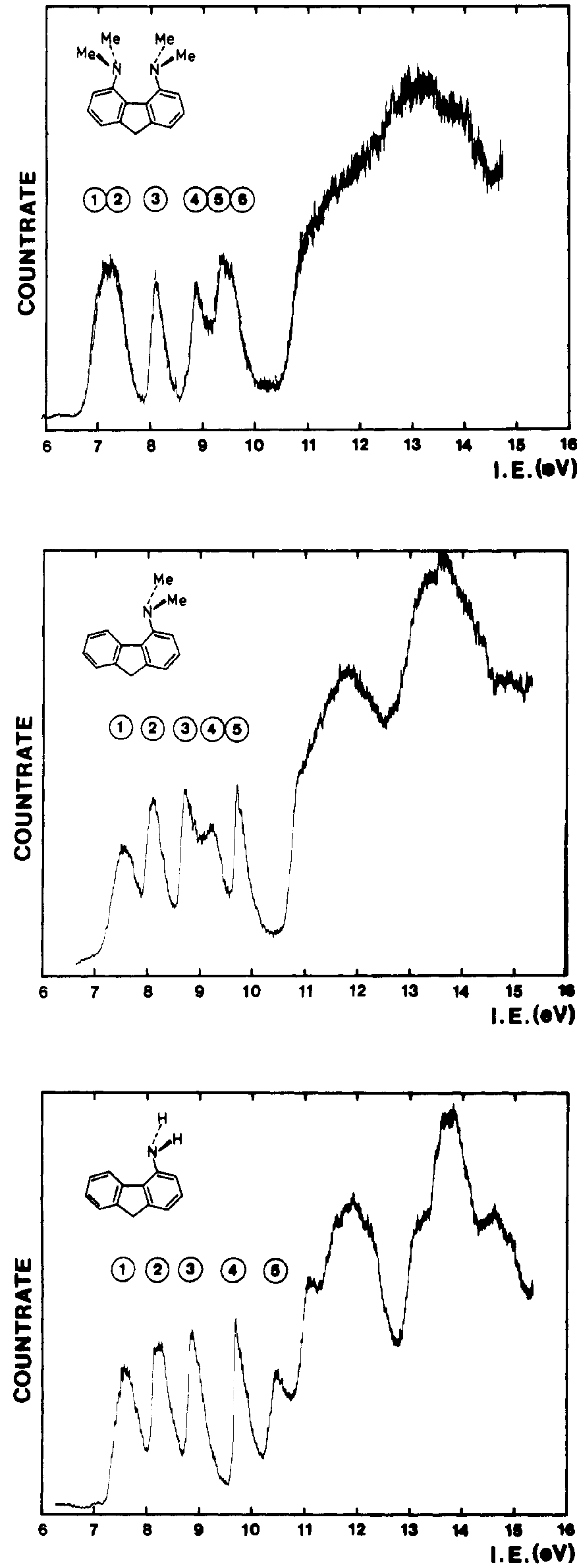

Figure 1. He(I) PE spectra of 1, 3, and 4.

The application of (1) to 1 yields the following values for the π MO's:

$$\epsilon_j' \text{ (eV)}: -7.39, -8.17, -8.57, -9.60$$

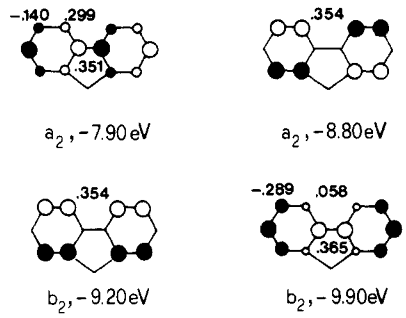

Figure 2. Schematic representation of the four highest occupied orbitals of fluorene. The orbital energies given are the negative values of the ionization energies. The HMO coefficients are those obtained for biphenyl.

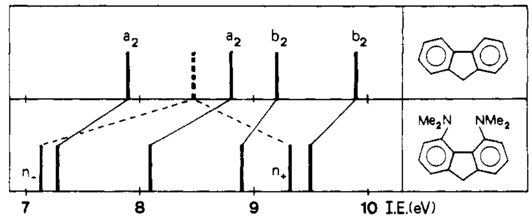

Figure 3. Correlation between the first bands of the PE spectra of biphenyl and 4,5-bis(dimethylamino)fluoren (1). The broken line gives the basis orbital energy of the dimethylamino groups in 1.

By comparison with the ionization energies of 1 we therefore assign bands 2–4 and 6 to ionization events out of π-orbitals localized at the fluorene moiety. Bands 1 and 5 are due to ionizations from the lone pair combinations n_- and n_+ defined in eq 2. In these expressions the sp^3 lone pairs at the nitrogen centers are represented by n_a and n_b.

$$n_- = \frac{1}{2^{1/2}}(n_a - n_b) \qquad n_+ = \frac{1}{2^{1/2}}(n_a + n_b) \qquad (2)$$

If we adopt the assignment just discussed and presented in Table I we find a through-space interaction between n_+ and n_- in 1 by 2.2 eV. With this finding in line is the splitting found for **2** which amounts to 2.0 eV. The larger value found for 1 corroborates the smaller N–N distance in 1 suggested by molecular models and the larger pK_a value.

In Figure 3 we have correlated the first ionization energies of fluorene with those of 1. The basis orbital energy of the dimethylamino group is indicated by a dotted line. To assign the PE spectra of **3** and **4** we also start with the basis orbital energies of **5**. The inductive perturbation of an amino group ($\delta\alpha$ = 0.5 eV)[6] and a dimethylamino group ($\delta\alpha$ = 1.9 eV)[6] is taken care of by a first-order perturbation treatment according to (1), starting with the wave functions presented in Figure 2.

The effect of conjugation between the substituent and the π-system is described by the resonance integral B_{CN}

$$B_{CN} = \langle \varphi_C | H | \varphi_N \rangle$$

between the AO's centered at the C and N atoms. In the case that the NR$_2$ group is twisted by θ around the CN bond we approximate the resonance integral by

$$B_{CN}(\theta) = B_{CN}(0°) \cos \theta$$

For $B_{CN}(0°)$ we adopt a value of −2.4 eV[6] which has been used to describe several amino derivatives of benzene and naphthalene.

The basis energies A_N are defined by

$$A_N = \langle \varphi_N | H | \varphi_N \rangle$$

For the dimethylamino group we adopt a value of −8.7 eV[6]

Table II. Calculated Orbital Energies of 1, 3, and 4

compd	$-\epsilon$(ZDO)	$-\epsilon$(MINDO/3)
1	(7.14 (n))	7.81 (a_2, π)
	7.39 (π)	8.01 (b_1, n_-)
	8.17 (π)	8.54 (b_2, π)
	8.57 (π)	8.75 (a_2, π)
	(9.34 (n))	8.88 (a_1, n_+)
	9.60 (π)	9.73 (b_2, π)
3	7.42 (π)	7.83 (π)
	8.09 (π)	8.43 (π)
	8.63 (n)	8.86 (π)
	9.41 (π)	9.03 (n)
	9.88 (π)	9.76 (π)
4	7.62 (π)	7.71 (π)
	8.41 (π)	8.43 (π)
	8.92 (π)	8.92 (π)
	9.78 (π)	9.72 (π)
	11.36 (π)	9.86 (π)

and for the amino group −10.6 eV.[6] Assuming a rotation of 40° around the CN bond in 3 and 0° in 4, we obtain the values shown in Table II. The agreement between experiment and ZDO calculation is fairly good. Our assignment given in Table I is based on the ZDO results.

b. Semiempirical Calculations. To derive the orbital sequence in 1, 3, and 4 by semiempirical methods we have used the MINDO/3 model.[7] For 4 we minimized all geometrical parameters with respect to the heat of formation. In the case of 1 and 3 the distances and angles for the fluorene skeleton were minimized as for 4 while for the dimethylamino groups in 1 and for the dimethylamino group in 3 we assumed a rotation of 90° and 40° out of the π-plane, respectively. The energy levels obtained are listed in Table II.

In the case of 3 and 4 the agreement between the results of the ZDO calculations and of the semiempirical calculations is good. For 1, however, the large split between the two lone-pair combinations, n_+ and n_-, as predicted by the ZDO model is not reproduced satisfactorily by the MINDO/3 method. The energies of the π-orbitals on the other hand are predicted by MINDO/3 close to those obtained by the ZDO model. We ascribe this discrepancy due to our assumed geometry of the dimethylamino groups.

Experimental Section

Compounds 3 and 4 were prepared according to the literature.[8] The synthesis of 1 has been reported recently.[1]

The PE spectra of the pure samples were recorded on a Perkin-Elmer PS 18 and a Leybold Heraeus UPG 200 photoelectron spectrometer equipped with a He(I) light source. The spectra were recorded at 73 °C (1), 58 °C (3), and 105 °C (4). The calibration has been carried out with Ar and Xe. A resolution of ±0.04 eV was achieved for the single bands and of ±0.1 eV for the shoulders.

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Supplementary Material Available: A listing of the calculated or assumed geometrical parameters for 1, 3, and 4 (2 pages). Ordering information is given on any current masthead page.

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High-Field Rapid Injection NMR: Observation of Unstable Primary Ozonide Intermediates[1]

John F. McGarrity* and Jacques Prodolliet

Institut de chimie organique, Université de Lausanne, CH-1005 Lausanne, Switzerland

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A "rapid injection" NMR system is described for use on a 360-MHz superconducting spectrometer. The major advantages of the high-field system over our original system are increased sensitivity, resolution, and rapidity. The technique was used to study the ozonolysis of tetramethylethylene and (briefly) *cis*-but-2-ene, particularly the decomposition of the corresponding primary ozonides 2 and 4, with half-lives of 0.74 and 0.06 s, respectively, at −92 °C. It was found that the decomposition of 2 in CD_2Cl_2 (a) had $\Delta H^{\ddagger} = 39$ kJ/mol and $\Delta S^{\ddagger} = 28$ J/(mol K), (b) was unaffected by the presence of TCNE, but (c) was acid-catalyzed. The effects of substituents, solvent, and acid catalysts on the decomposition of primary ozonides are discussed.

Introduction

We have recently described the rapid injection NMR (RINMR) technique for the observation (at 60 MHz), of short-lived organic intermediates.[2] As a kinetic application we have measured the hydrolysis rates of very reactive methylating agents.[3] The RINMR method involves injection of a small volume (typically 10–15 μL) of a premagnetized reagent solution into a standard volume (300 μL) of a substrate solution already spinning in the NMR probe. The computer acquisition system is automatically triggered by the injection. The advantages of this con-

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